133

INVESTIGATION OF SULPHUR VAPOUR TECHNIQUES IN EXPLORATION GEOCHEMISTRY

by

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ABSTRACT

A detailed description of previous work in sulphur vapour geochemistry using sulphur dioxide and hydrogen sulphide as indicators of concealed sulphide mineralizations is given, followed by a presentation of general geochemical data on sulphur and its abundance in the lithosphere, biosphere, hydrosphere, atmosphere and the anthroposphere.

Based on literature information that sulphur dioxide and hydrogen sulphide could successfully be used in mineral exploration, an investigation of sensitive analytical methods for these two compounds was carried out. Two specific, manual wet chemical, colorimetric methods were finally selected. A presentation of the development of procedures making the methods acceptable for field-use is given followed by a description of field sampling techniques and a discussion of the results obtained.

The discouraging results obtained using sulphur dioxide and hydrogen sulphide as pathfinders for oxidizing sulphide deposits led to an investigation of other possible sulphur gases. Gas chromatography together with a flame photometric detector fitted with a filter, specific for sulphur, was found to be the most promising analytical system available.

Due to the diversity and high reactivity of sulphur gases, separation of sulphur dioxide from hydrogen sulphide carbonyl sulphide from hydrogen sulphide and carbon disulphide from dimethyl sulphide has been extremely difficult to obtain using one gas chromatograph column, when the components are present in sub-ppm concentrations. A description is given of a procedure, giving the desired performance with well differentiated peaks in a reasonable time for each analysis. Using this procedure, six organic and inorganic sulphur compounds including carbonyl sulphide, hydrogen sulphide, sulphur dioxide, carbon disulphide, dimethyl sulphide and dimethyl disulphide can be separated from each other, several of which were found to be liberated from oxidizing sulphides under laboratory conditions.

Techniques for the collection and transport of samples for subsequent analysis in the laboratory on the gas chromatograph are described, followed by a discussion of the results obtained.

Finally, conclusions are drawn concerning the use of sulphur vapours in mineral exploration.

ACKNOWLEDGEMENTS

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INVESTIGATION OF SULPHUR VAPOUR TECHNIQUES IN EXPLORATION GEOCHEMISTRY

Introduction

One of the more difficult problems in mineral exploration is locating ore deposits concealed beneath, exotic overburden or barren cap-rocks under conditions where conventional geochemical survey techniques fail to yield a surface expression of the mineralization.

In recent years some attention has been given to the possibility of using the inherent mobility of vapours derived from mineral deposits to pass upwards through rock and overburden and to methods of detecting these vapours at or near the surface as a prospecting technique.

The present research forms part of a broad-based investigation of vapour geochemistry in mineral exploration funded by the Mineral Industry Research Organisation (MIRO) and is concerned primarily with the investigation of sulphur gases emanating from concealed metalliferous sulphide deposits. Other aspects of this overall programme include studies of the halogens, mercury, oxygen/carbon dioxide ratios, radon etc. which are being studied by other members of the research team at Imperial College.

The writer's research was divided into three sections: (1) a review of previous literature concerning the application of sulphur gases in mineral exploration and a comprehensive study of the literature bearing on sulphur gases in the natural environment, (2) the development of appropriate field techniques for the detection of sulphur gases and (3) the testing of these techniques over shown sulphide deposits in the field.

It is necessary at this stage to state that the research has demonstrated that the previous work, which indicated that sulphur dioxide and hydrogen sulphide could be used as indicator gases appears to have little general application in exploration. Although negative in this respect the results nonetheless have a positive value in disproving this concept; secondly, towards the end of the project, preliminary experimental work using gas chromatography indicated that other sulphur gases, notably carbonyl sulphide, carbon disulphide and dimethyl disulphide could have far greater potential. These preliminary experiments have laid the foundation for further research on these gases as part of the overall MIRO project.

Before outlining the relevant factors of sulphur vapour geochemistry in Chapter 2, it is necessary to outline in some detail the previous work on sulphur geochemical techniques applied to mineral exploration which formed the starting point for the present investigations.

CHAPTER 1

PREVIOUS WORK ON SULPHUR VAPOUR GEOCHEMISTRY APPLIED TO MINERAL EXPLORATION

In the Soviet Union, vapour geochemistry was introduced in 1932 by Sokolov, who suggested the use of gases in exploration for petroleum (Elinson, 1970). Thirty years later, A. Kahma started his experiments using dogs in the search for weathering sulphide boulders (A. Kahma et al, 1975). In the last 10 - 15 years, a number of papers have been published in vapour geochemistry, giving information on a variety of gases such as mercury, carbon dioxide, oxygen, helium, radon, halogens, hydrocarbons, noble gases and sulphur gases and the usefulness of these gases in mineral exploration.

The basic idea of the vapour geochemical exploration technique is to examine the composition of the soil atmosphere or the free atmosphere above ore deposits, fracture zones etc. and to compare this with background. It is generally believed that the former contains an altered gas composition due to chemical processes and bacteriological activities. Elinson (1970) illustrates this in Fig. 1.1.

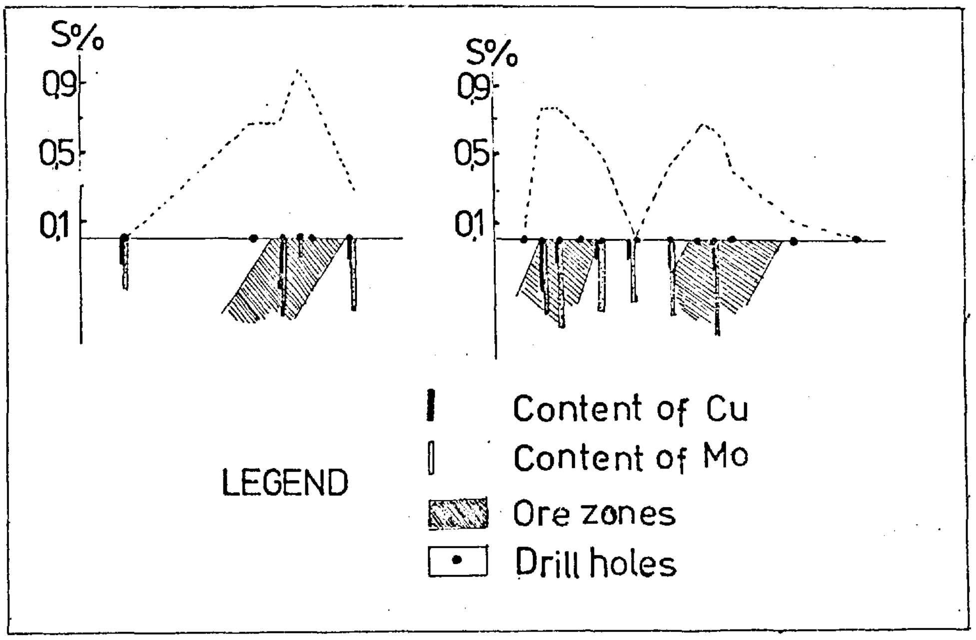

Fig. 1.1 Distribution of sulphur gases in relation to copper-molybdenum deposits in skarns and epidosites. (Elinson, 1970)

Shipulin and his co-workers have been active in southern Russia, where they have been investigating the relationship between copper-molybdenum sulphide deposits and generated gases. A correlation as illustrated in Fig. 1.2 was found to exist between hydrogen sulphide and molybdenum, while no correlation between sulphur gases and pyrite could be proved (Shipulin et al, 1973). The same investigators state that under certain conditions pyrite and sulphur gases do not have any relationship. Elinson (1970) has been working in the same part of Russia and he suggests that hydrogen sulphide and sulphur dioxide can be associated with copper-molybdenum deposits containing pyrite, chalcopyrite and molybdenum.

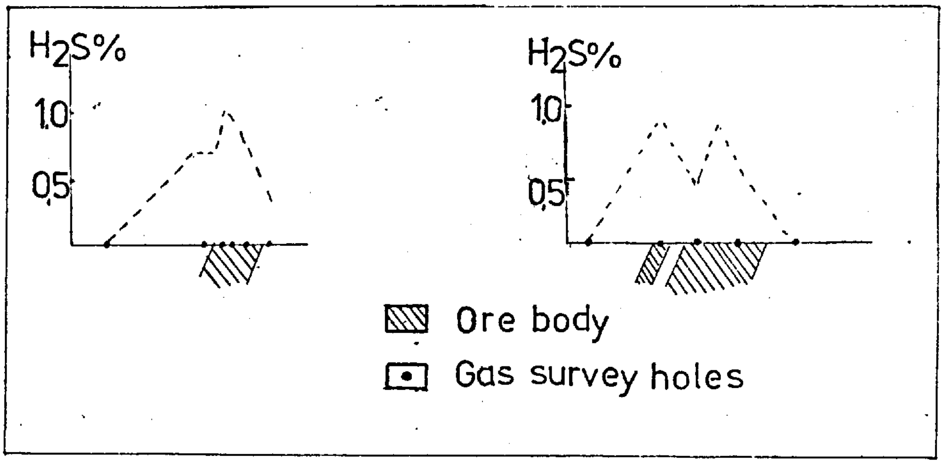

Fig. 1.2 H_2S content over copper-molybdenum ore bodies in skarns and epidosites. (Shipulin et al, 1973)

Shipulin et al (1973) state that pyrite is more easily oxidized than chalcopyrite and molybdenite. According to Elinson (1970) there are complications of a survey in slowly oxidizing sulphides such as those containing molybdenum.

Shipulin et al (1973) show the composition of the subsoil atmosphere down to 1.5 - 2.5 m over a copper-molybdenum deposit in their investigation area (Table 1.1).

Table 1.1 Composition of the subsoil atmosphere over a sulphide ore deposit.

GAS	%
Oxygen	12 - 21
Nitrogen	75 - 80
Carbon dioxide	0 - 4
Hydrogen sulphide	0 - 0.8
Sulphur dioxide	0 - 0.1
Carbonyl sulphide	0 - 0.5
Hydrogen	0 - 0.5
Methane	0 - 0.5

The figures for the sulphur gases appear suspect since the background values for these in soils are expected to be in the lower ppb range. Bristow and Jonasson (1972) state that sulphur dioxide anomalies can be detected if the sulphur dioxide concentration exceeds the background by 2 - 6 times. Rouse and Stevens (1971) detected concentrations of about 50 ppb sulphur dioxide over sulphides and Peters (1973) recorded detectable levels of sulphur dioxide in soil over sulphide-bearing deposits. As compared with the composition of the atmosphere of depths, there are differences because of bacterial, chemical and meteorological factors in the oxidation zone. No sulphur gases were detected by Rouse and Stevens (1971) in the background areas, suggesting that these gases are derivation products of oxidation processes on sulphide deposits.

The oxidation of sulphides is described more in detail elsewhere in this thesis. However, as all work concerning sulphur vapours in mineral exploration is related in one way or another to this process, it is necessary to say a few words about this phenomenon at this stage.

Sulphides are oxidized, chemically or by bacteria, resulting in the formation of sulphates and if water is present, sulphuric acid. The oxygen in the close vicinity of the deposit is consumed and bound to the sulphates and sulphuric acid, causing a decrease in the concentration of oxygen. The sulphuric acid attacks sulphides, sulphates and carbonates (if present) forming hydrogen sulphide and carbon dioxide.

Shipulin et al (1973) claim that only sulphates of Cu and Mo are bacterially reduced, while gypsum and iron-sulphates remain intact. The same investigators further suggest that the activity of reducing bacteria is decreased if Na, K, Ca, Mg and Fe are present, while Cu, Mo, Ni, Zn and Pb do not affect the production of hydrogen sulphide. Kadota and Ishida (1972) have shown that this gas is produced by microbes. Banwart and Bremner (1975) could not, however, detect hydrogen sulphide formed by microbiological activities. They say that the microbes may produce hydrogen sulphide, but that it might be sorbed by soils resulting in its absence in the free atmosphere. Hydrogen sulphide, besides being formed from sulphates, can also be a disintegration product from organic sulphur compounds in e.g. vegetation, making it less suitable to use sulphur gases in areas with an abundant flora (Shipulin et al, 1973; Kadota and Ishida, 1972). Naturally occurring sulphur dioxide is an oxidation product of hydrogen sulphide (Rasmussen, 1974).

Many other workers as, e.g. Glebovskaya and Glebovskii (1960) mention that the overburden above sulphide mineralization may be enriched with hydrogen sulphide and sulphur dioxide due to the oxidation of sulphides. Rouse and Stevens (1971) claim to have detected sulphur dioxide over porphyry copper deposits in North America. Bristow and Jonasson (1972) claim that any sulphide deposit can generate sulphur dioxide only if it is oxidized. Ovchinnikov (1972) mentions hydrogen sulphide and sulphur dioxide to be products from oxidation processes and Peters (1973) claims to have shown the presence of sulphur dioxide over sulphide mineralizations in Newfoundland.

The use of dogs for prospecting for weathering sulphide boulders is closely related to sulphides in the oxidation zone. This new prospecting method will be briefly described below.

In glacial terrain, as found in the Scandinavian countries, boulder tracing is an important prospecting tool in the search for mineral deposits. Mostly an overburden of till, glaciofluvial material, soil and vegetation covers the boulders. Weathering sulphides evolve sulphur gases which can be smelt by human beings. It was suggested by A. Kahma in Finland (1962) that dogs with their finer sense could smell sulphide-rich boulders or mineralizations through the overburden (J.S. Brock, 1972; A. Kahma et al, 1975). It has been shown in a later work by Kahma, that the major compound released from the weathering boulders, was sulphur dioxide and that the other gases were hydrogen sulphide and carbonyl sulphide. A fourth unknown gas was also detected (A. Kahma et al, 1975). Successful results using dogs for prospecting have also been reported from Sweden (G. Nilsson, 1971) and Canada (J.S. Brock, 1972). In the former country a dog was able to find a boulder in scree 1 m below the surface, and the Finns report one case, when a dog detected sulphides at a depth of 3 m (J.S. Brock, 1972).

Besides the use of gases in detecting mineral deposits, it has been shown by Ovchinnikov (1972), Bristow and Jonasson (1972), Shipulin et al (1973), Kulikova (1960), Ernst (1968) and Headlee (1962) that gases might be useful in the application for the discovery of fractures, faults and joints, concealed by overburden, since gases such as helium, radon and mercury vapour generated at depth tend to migrate to systems of fractures and to zones of intensive tectonics. Ovchinnikov illustrates the presence of deep-origin gases (He) close to fractures in Fig. 1.3.

Many papers reveal that sulphur gases are generated from weathering sulphides, on or below the surface, where they can in many cases, be detected with sensitive vapour sensing techniques, dogs or other methods. Peters (1973) and Meyer (1973) report that microwave-induced argon plasma emission analysis may be used in mineral exploration to detect sulphur related to oxidizing sulphide deposits. Problems with the analysis of sulphur gases have been reported by Glebovskaya and Glebovskii (1960), who failed to use hydrogen sulphide and sulphur dioxide in exploration, despite the fact that they could

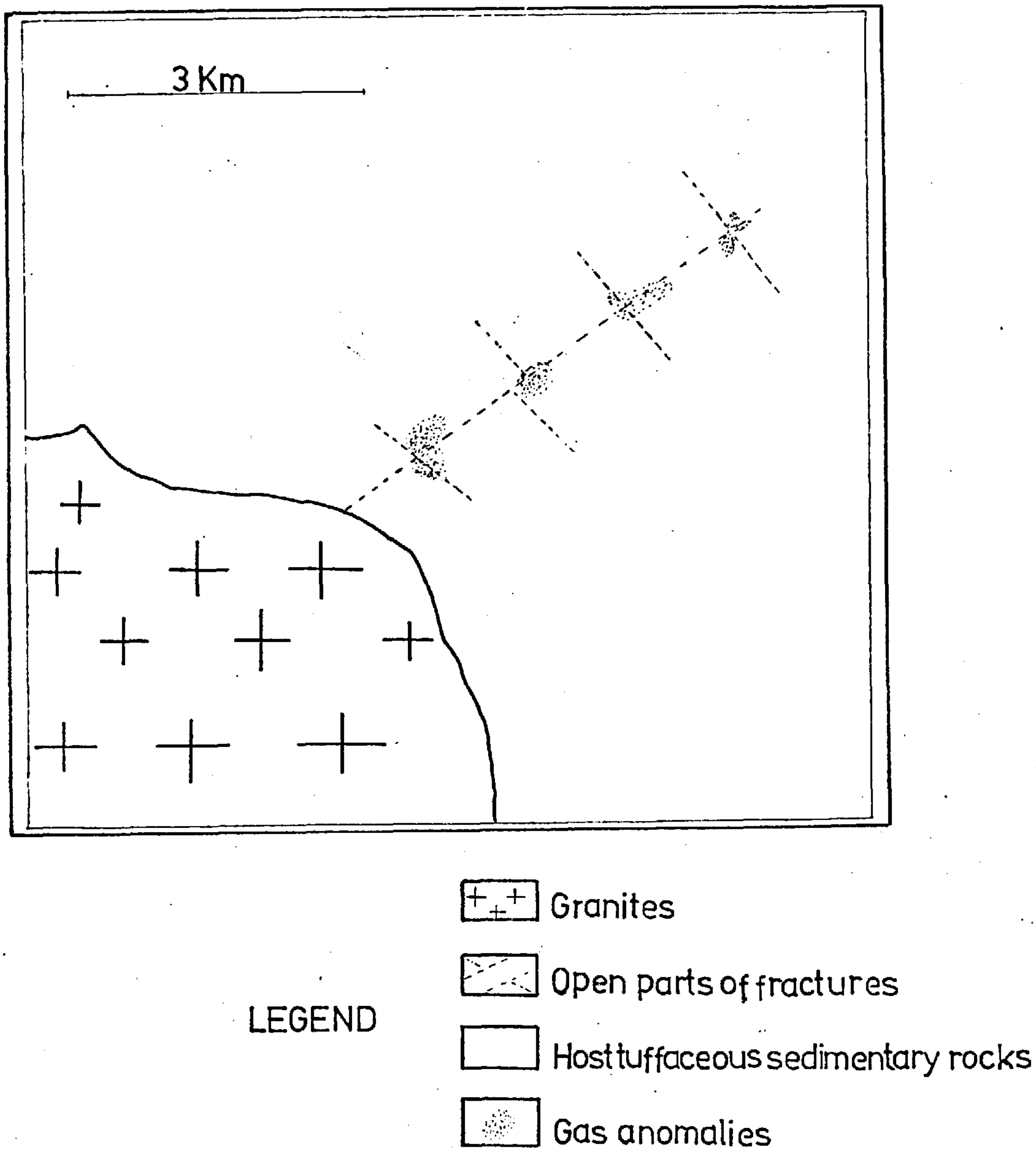

Fig. 1.3 Gas anomalies (Ovchinnikov, 1972)

smell these compounds. Rouse and Stevens (1971) have not published any paper describing the method used in their exploration work in Arizona (Coope, 1973). Difficulties with the analysis and interpretation of anomalies are the main negative aspects of this new aid in prospecting. A summary of unfavorable conditions for using sulphur gases in exploration, suggested in the literature, are listed below:

(1) Low intensity of oxidation
(2) Mineralization is below the groundwater level
(3) Mineralization is situated at a too great a depth
(4) High moisture content in the overburden
(5) Abundant vegetation and organic matter in soil or overburden.

On basis of the positive information given in the literature using sulphur dioxide and hydrogen sulphide in exploration for concealed oxidizing sulphide-bearing mineralizations, an extensive study on the geochemistry of sulphur was carried out, followed by practical work with reference to these two gases and their role in exploration geochemistry.

CHAPTER 2

SULPHUR GEOCHEMISTRY

During the course of the preliminary literature review over 300 papers relating to sulphur and sulphur gases were extracted (see Appendix). Only those which are relevant to the present investigation are given in this section and are listed in the references.

2.1 Introduction

Sulphur (atomic number 16) is in group VIA of the periodic table together with oxygen, selenium, tellurium and polonium. Some of its properties are: atomic weight (32,064), density (2.07), hardness (1.5-2.5), colour (yellow), melting point (113°C) and boiling point (445°C). Sulphur is orthorombic below 96°C and monoclinic above. Four stable isotopes ^{32}S, ^{33}S, ^{34}S and ^{36}S exist. Their abundancies are 95.018%, 0.75%, 4.215% and 0.017 respectively (Wedepohl, 1971). In addition, another six unstable (radioactive) isotopes are reported in the literature. Sulphur is a polyvalent non-metallic element which reacts with almost all elements (exceptions are iodine, nitrogen and the noble gases) owing to its many valence states. The most common sulphur compounds and their valences are: sulphate (+6), sulphite (+4), thiosulphate (+6, -2), elemental sulphur (0), disulphide (-1) and sulphide (-2).

Most characteristic of sulphur gases are their lack of colour and their disagreeable odour, revealing their presence even in low concentrations. Most of them are very poisonous. Hydrogen sulphide is more dangerous than sulphur dioxide and carbonyl sulphide has been claimed to be even more poisonous than hydrogen sulphide. It has been found that the odour of hydrogen sulphide is noticeable at 10-25 ppb, unpleasant at 3-5 ppm and hard to stand at 20-30 ppm. The smell of hydrogen sulphide is less intensive at about 200 ppm owing to the fact that at high concentrations it deadens the sense of smell (Hampel, 1968 and many others). Irritation of sulphur dioxide is noticed at 6-20 ppm. Plants are damaged at 2-7 ppm levels (Smith et al, 1961; Hampel, 1968 and many others). Sulphur dioxide in combination with dust or fog leads to formation of sulphur trioxide, which is a danger to all living matter.

2.2 Geochemical Distribution of Sulphur

2.2.1 Introduction

Sulphur is one of the few elements found in the Earth's crust in elemental form. It is widely distributed and is present in all geochemical spheres. The average sulphur content of the crust is 520 ppm, which places it among the most common elements in the lithosphere (Mason, 1958). In igneous rocks, sulphur is the fourteenth or fifteenth most abundant element, while in the Universe it is estimated to be the ninth. Over the Earth it is present in the lithosphere, pedosphere, hydrosphere and atmosphere.

2.2.2 The lithosphere

The abundance of sulphur in igneous and sedimentary rocks are given by many workers. The main sources for the figures below are Rankama and Sahama (1950) and Krauskopf (1967).

In the lithosphere, sulphur occurs as elemental sulphur, sulphides and sulphates. Many times these compounds are found in high concentrations. A more extensive description of these deposits in which sulphur is involved is presented

Table 2.1 Abundance of sulphur in rocks.

	Concentration (ppm)
Igneous Rocks	260
mafic	300
intermediate	200
acidic	300
Sedimentary Rocks	300
sandstone	240
shale	270

below. Naturally occurring sulphur gases are sometimes associated with weathering sulphides, putting this group of minerals in priority when working with sulphur vapour geochemistry in mineral exploration (Shipulin et al, 1973 among others). The percentage sulphur in some common sulphides and sulphates are shown in Table 2.2.

Table 2.2 Common sulphur-bearing minerals showing composition and sulphur content.

	Sulphides	
Mineral	Composition	S(%)
Pyrite	FeS_2	53.4
Molybdenite	MoS_2	40.1
Pentlandite	$(Fe,Ni)_9S_8$	36.0
Chalcopyrite	$CuFeS_2$	35.0
Covellite	CuS	33.6
Sphalerite	ZnS	33.0
Bornite	Cu_5FeS_4	35.5
Chalcocite	Cu_2S	20.2
Arsenopyrite	FeAsS	19.7
Galena	PbS	13.4

Table 2.2 (continued)

Sulphates		
Mineral	Composition	S(%)
Anhydrite	$CaSO_4$	23.5
Gypsum	$CaSO_4$ x $2H_2O$	18.6
Alunite	$KA\ell_3(SO_4)_2(OH)_6$	15.4
Barite	$BaSO_4$	13.7
Anglesite	$PbSO_4$	10.6

2.2.2.1 Mineral deposits in which sulphur is associated

In the lithosphere, sulphur may occasionally accumulate and form deposits of economical importance. Sulphur may occur as elemental sulphur, various sulphides and various sulphates. In addition sulphur compounds are found in coal, petroleum and natural gas.

Elemental sulphur is found in many different environments and deposits:

1. Volcanic

A In recent volcanic regions elemental sulphur is formed in various ways: (1) as a sublimation product from volcanic gases and (2) as a product from chemical reactions such as:

$$H_2S + 2SO_2 \rightarrow H_2SO_4 + 2S$$
$$2H_2S + O_2 \rightarrow 2H_2O + 2S$$
$$3SO_2 + 2H_2O \rightarrow H_2SO_4 + S$$

B In districts with recent or ancient thermal springs. Origin and genesis of sulphur may be contributed to:

(1) the oxidation of hydrogen sulphide, (2) bacterial activity and (3) the reaction between suspended $CaCO_3$ and H_2S, resulting in $Ca(SH)_2$.

2. Sedimentary

A In sedimentary strata of Tertiary age, elemental sulphur is associated with gypsum and limestone.

B Normally in porous gypsum or calcite units in the cap-rocks of salt domes (this sulphur may be the result of the reducing influence of bacteria on sulphates).

C In sediments, where microbiological activities produce sulphur from acid sulphur gases derived from the decomposition of organic matter.

The sulphides, including the sulphosalts consist of sulphur and either a metal or non-metallic element or elements such as Fe, Ni, As, Cu Pb, Zn, Mo and Hg. More than one hundred elements are known and most of them form sulphides or polysulphides with sulphur. Exceptions are nitrogen, the noble gases and iodine as mentioned elsewhere. The bonding between the elements in the sulphides may be ionic, covalent or partial metallic.

In sulphide deposits, the sulphide minerals may occur as concentrated accumulations in a host rock, igneous or sedimentary, as impregnations in rocks or as minerals in veins. Most of the sulphide minerals are primary, though some always occur as secondary compounds. Copper sulphide minerals are often found as secondary enrichments; chalcopyrite for instance may appear either as a primary or a secondary mineral owing to chemical alteration subsequent to the formation of the deposits themselves.

Sulphate minerals are found in many different deposits such as: evaporites (as secondary minerals), veins (as primary minerals) and in the oxidation zone of ore bodies (as secondary minerals). Evaporation, a sedimentary process, proceeds rapidly in warm and arid environments. The most important minerals found in this type of deposit are: gypsum, anhydrite (calcium sulphates), kieserite (magnesium sulphate) and sodium and potassium sulphates. Gypsum and anhydrite are the most important economically and most abundant. A common sulphate mineral in veins is barite, which also occurs in replacement and residual deposits. In the oxidized zone of lead-bearing ore deposits, anglesite may occur.

2.2.3 The pedosphere

Rocks and sulphide minerals are the main sources of sulphur in soils. In the pedosphere, sulphur is present in rather small amounts, existing in both organic and inorganic forms. The former is more abundant. Freney (1967) reports that less than 1% of the total sulphur in surface soils from Australia occurs as reduced inorganic sulphur. Sulphate accounts for the major part of the inorganic sulphur in most soils. Under anaerobic conditions, sulphides are the dominating group, while in an aerobic environment, sulphates are more abundant. Elemental sulphur and organic sulphur compounds exist in some natural environments and can be found in peat and coal. It is pointed out in another section of this thesis that sulphur undergoes many transformations owing to chemical and microbiological processes. These transformations of sulphur depend on soil type and soil conditions and affect soil colour, soil reaction and availability of plant nutrient elements and are thus very important in agriculture.

Different soil types contain various amounts of sulphur compounds and of total sulphur. In podzol and chernozem, most of the sulphur is organic. Chao et al (1962) found that some of the sulphur is absorbed by hydrous Aℓ-Fe oxides in the mineral-rich part. Peters (1973) reported from his investigation of organic and peaty soils of podzolic type in Newfoundland 500-2000 ppm sulphur in the background and 50-500 ppm in the mineral-rich part.

It has been known for a long time that sulphur is an important component in the nutrition of plants. In most plants, the amino-acids, methionine and cysteine, account for 90 percent of total sulphur. It has been shown by chromatographic analysis of acid hydrolysates of soils that sulphur-containing amino-acids exist in soils, bonded to soil particles etc. Tabatabai and Bremner (1972) say that there exists no clear evidence that organic sulphur occurs in the form of organic sulphates, since attempts to separate ester sulphates from soils have been unsuccessful. It is however believed, that organic sulphur not bonded to carbon, exists in the form of ester sulphates (as e.g. polysaccharides).

Tabatabai and Bremner (1972) examined soils in Iowa, U.S.A., and found that the existing inorganic sulphur occurred entirely as sulphate. They found neither sulphides nor inorganic non-sulphate sulphur. 1 - 5 percent of the total sulphur consisted of sulphates. The rest was found to be organic sulphur.

Other important sources of sulphur are: (1) weathering sulphide deposits, (2) precipitation of atmospheric sulphur compounds and direct adsorption of these by grass and soil, (3) decomposition of biological material and (4) fertilizers.

In the improvements of agriculture, fertilizers in the form of sulphates and elemental sulphur, directly available to plants, are added to soils. On a global scale, these are insignificant in the sulphur cycle, since their contribution of sulphur is rather small.

All the other sources and their products are considered in other sections of this thesis. For vapour geochemistry and its utilization in mineral exploration these are important, since emitted compounds are volatile in many cases, resulting in difficulties when interpreting origin of sulphur compounds detected in the soil atmosphere.

A list of possible sulphur compounds in soil is finally presented.

Table 2.3 Sulphur compounds in soil.

A <u>Solid</u>

1	Sulphides
2	Sulphates
3	Elemental sulphur
4	Organic sulphur compounds
a	amino-acids
b	proteins
c	enzymes

Table 2.3 (continued)

	B Liquid
1	Sulphuric acid
	C Gas
1	Hydrogen sulphide
2	Methyl mercaptan
3	Dimethyl sulphide
4	Dimethyl disulphide
5	Carbonyl sulphide
6	Sulphur dioxide
7	Carbon disulphide

2.2.4 The hydrosphere

The hydrosphere includes all water - fresh, salt and solid - on the surface of the Earth. In the lithosphere sulphur occurs mainly as sulphides. These may be oxidised to sulphates which are available to plants and microorganisms. The more soluble sulphates are carried away by groundwater, resulting in more or less high concentrations in rivers, lakes and oceans.

In seawater, sulphur is one of the major dissolved constituents being exceeded in abundance only by oxygen, hydrogen, chlorine and sodium. The principal constituents are shown by Mason (1958) and Krauskopf (1967):

Table 2.4 Principal constituents of dissolved substances in sea water

Substance	Concentration (ppm)
$C\ell^-$	18980
Na^+	10556
SO_4^{2-}	2649
Mg^{2+}	1272
Ca^{2+}	400
HCO_3	140

The average abundance of sulphur in seawater and river water is 885 ppm and 112 ppm respectively (Mason, 1958; Krauskopf, 1967). The sources of the sulphates in the oceans are mainly: (1) direct derivation from volcanic activity, (2) oxidation of sulphides and (3) oxidation of volcanic gaseous sulphur compounds. In freshwater, the sources of the sulphates are: (1) oxidation of sulphides and (2) precipitation from the atmosphere. Sulphates in the oceans may be removed in two ways: (1) it can escape to the atmosphere, and gradually be transported to the land and (2) it can be reduced to sulphides.

It has been observed that the concentration of hydrogen sulphide increases whereas the concentration of sulphate decreases going from surface to the bottom of oceans.

Hydrogen sulphide and sulphur dioxide are soluble gases. One volume of water at 20°C dissolves 2.6 volumes of the former gas and 36 volumes of the latter. Table 2.5 shows the concentration of gases in seawater.

Table 2.5 Dissolved gases in seawater (Mason, 1958)

Compound	Concentration (mℓ/ℓ)
Oxygen	0.9
Hydrogen sulphide	0-22 or more
Nitrogen	8.4-14.5
Total carbon dioxide	34-56

The sulphates may accumulate in brines and form considerable deposits of evaporites, which reducing sulphur bacteria may affect resulting in production of sulphur gases, which may be used as potential pathfinders for the deposits.

For the geochemist, the sulphates in freshwater might be useful in exploration for oxidizing sulphides (Hoag and Webber, 1976). The sulphate concentration is a good indication of the extend of oxidation of sulphides, provided that sulphide minerals are the primary source of sulphur. As we have seen, sulphates may also be precipitated from the atmosphere. In fresh natural waters, the sulphate content might be useful when estimating the degree of the oxidation of sulphides, provided that the atmospheric precipitation is low. If the sulphate content is less than 28 ppm, the rate of oxidation is none or very low, if it is between 28 - 160 ppm, some oxidation is taking place and if the sulphate content exceeds 160 ppm, the oxidation is extensive.

Finally, snow has been proved to be a useful medium for vapour geochemistry. Jonasson and Allan (1972) and Jonasson (1973) discuss the migration of trace metals in snow and their usefulness in mineral exploration. It has been suggested that gases, derived from concealed ore deposits, migrate through the snow on their way to the atmosphere - hence making it possible to do vapour investigations over frozen ground, bogs and lakes etc. during winter (Beck and Gingrich, 1976).

2.2.5 The biosphere

Sulphur is essential to life and is concerned with the metabolism of all classes of organisms. It is a component in amino-acids, proteins, fats etc.. Bacteria take part in the decomposition of organic matter, in which process sulphur gases may be evolved. In geochemistry, the role of bacteria in oxidation - reduction processes of sulphide/sulphate deposits is important.

In the lithosphere as well as in the pedosphere, primary sulphide minerals are converted by bacteria to sulphates. Organic sulphur compounds undergo further transformations before becoming available to plants. Microorganisms, plants and animals change this sulphate to many and varied compounds of which sulphur gases may interfere with the volatile sulphur compounds emanating from oxidizing sulphides, and therefore are of vital importance in sulphur vapour geochemistry (Headlee, 1962; Starkey, 1966; Lewis and Papawizas, 1970; Banwart and Bremner, 1975). Organic sulphur compounds may produce hydrogen sulphide as a decomposition product (Freney and Stevenson, 1966).

It has been believed that hydrogen sulphide is the major sulphur vapour, released through (1) reduction of sulphate and (2) desulphydration of organic sulphur compounds, from wet soils, swamps, muddy bottoms of lakes, coastal wet lands and estuaries and from the decomposition of living matter (Kadota and Ishida, 1972; Eriksson, 1963; Freney and Stevenson, 1966; Georgii, 1970; Junge, 1960; Robinson and Robbins, 1970). The measurements of hydrogen sulphide in Nature are few, owing to difficulties since no reliable available technique measuring low concentrations exists yet. Lewis and Papawizas (1970) and Banwart and Bremner (1975) could not detect hydrogen sulphide from decomposing organic matter in soils. As the biogenic production of gaseous sulphur compounds is of considerable importance in the sulphur cycle, much interest in these gases has been shown. Rasmussen (1974) suggests that dimethyl disulphide and related compounds dominate over hydrogen sulphide in the production of acid gases from wet areas. Other confirmations that organic sulphur emissions are more extensive than hydrogen sulphide are reported in the literature. Kadota and Ishida (1972), Lewis and Papawizas (1970), Banwart and Bremner (1975) and Lovelock and Maggs (1972) have found dimethyl sulphide, methyl mercaptan and dimethyl disulphide and, in one case, carbon disulphide among the volatiles derived from decaying organic materia.

The reasons why hydrogen sulphide was not detected by more than one of the workers just mentioned (Kadota and Ishida, 1972) might indicate that hydrogen sulphide is oxidized rapidly or adsorbed by soil particles. Smith et al (1973) mention the adsorption of sulphur dioxide, hydrogen sulphide and methyl mercaptan in soils (Fig. 2.1). Bremner and Banwart (1976) found that both wet and dry soils are able to adsorb

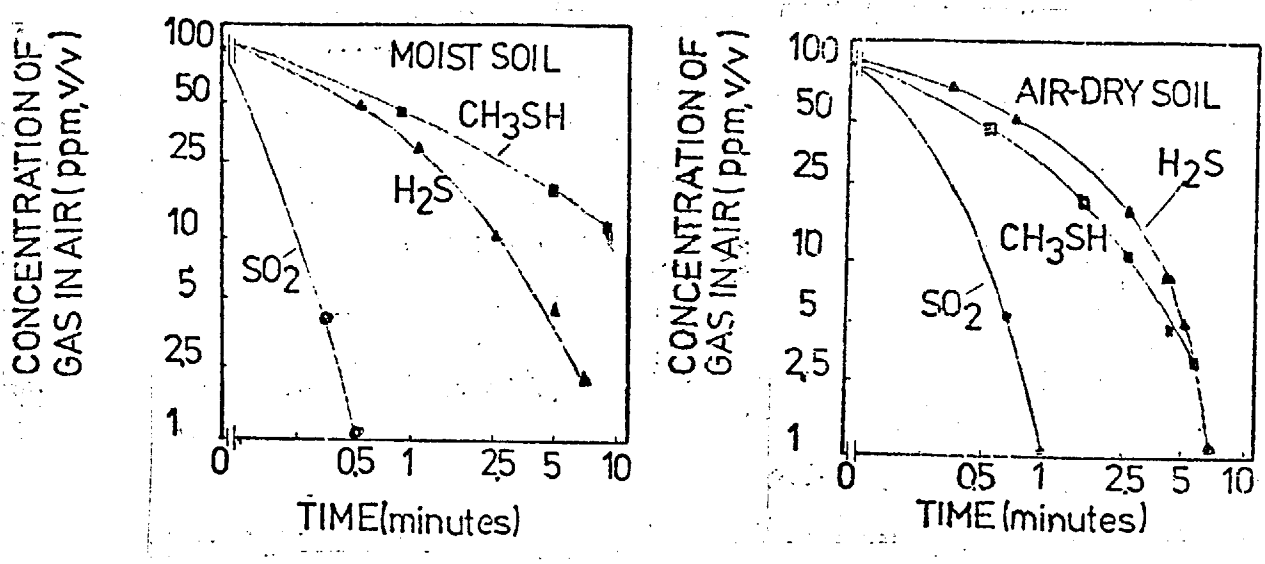

Fig. 2.1 Sorption of SO_2, H_2S and CH_3SH by soil from air initially containing 100 ppm (v/v) of these gases. (After Smith, Bremner and Tabatabai, 1973)

dimethyl disulphide, dimethyl sulphide, carbonyl sulphide and carbon disulphide. It was found in moist soils that carbonyl sulphide is more easily sorbed than carbon disulphide and the alkyl sulphides and that the sorption of hydrogen sulphide, sulphur dioxide and methyl mercaptan is more intensive than for the others. Terraglio and Manganelli (1966) claim that an increasing soil moisture content result in an increasing gas adsorption. The sorption of gases is treated in a later section of this thesis. The microbial transformation of sulphur may be grouped into four categories: (1) oxidation of sulphur and inorganic sulphur compounds, (2) reduction of sulphate, (3) assimilation of sulphur and (4) decomposition of organic sulphur compounds.

In addition to the biogenic emission of sulphur gases, these volatiles are released into the atmosphere from volcanoes, natural gas deposits, springs etc.. The weathering of sulphide mineralizations and dolomites and limestones contribute as well. These sources as well as their products will be described in a later section.

Many economically important deposits of derivates from the biosphere are to be found all over the Earth. The content of sulphur and sulphur gases are sometimes significant in some of them. Well-known examples are gas and petroleum. Hydrogen sulphide might be a useful pathfinder locating concealed accumulations of these deposits.

2.2.6 The atmosphere

The permanent degassing of the Earth contributes with a constant flow of sulphur-bearing gases and vapours to the atmosphere. The sources of the volatile sulphur compounds, escaping from the Earth to the atmosphere are: (1) volcanic activities, (2) natural gas deposits, (3) occlusions in rocks, (4) biochemical and non-biological processes on rocks and minerals and (5) industrial activities.

Sulphur gases form trace components which are always found in the atmosphere, even in remote areas (Ba Cuong et al, 1971; Weiss et al, 1971). The most common sulphur compounds in the atmosphere are: (1) sulphate aerosols and, (2) hydrogen sulphide, sulphur dioxide, sulphur trioxide, sulphuric acid and organic sulphur compounds.

In addition to gases and vapours, dust particles of varying origin are present. These have been collected, analysed and related to the underlying geology and geochemistry by Weiss (1971). Dust particles may act as catalysts in the

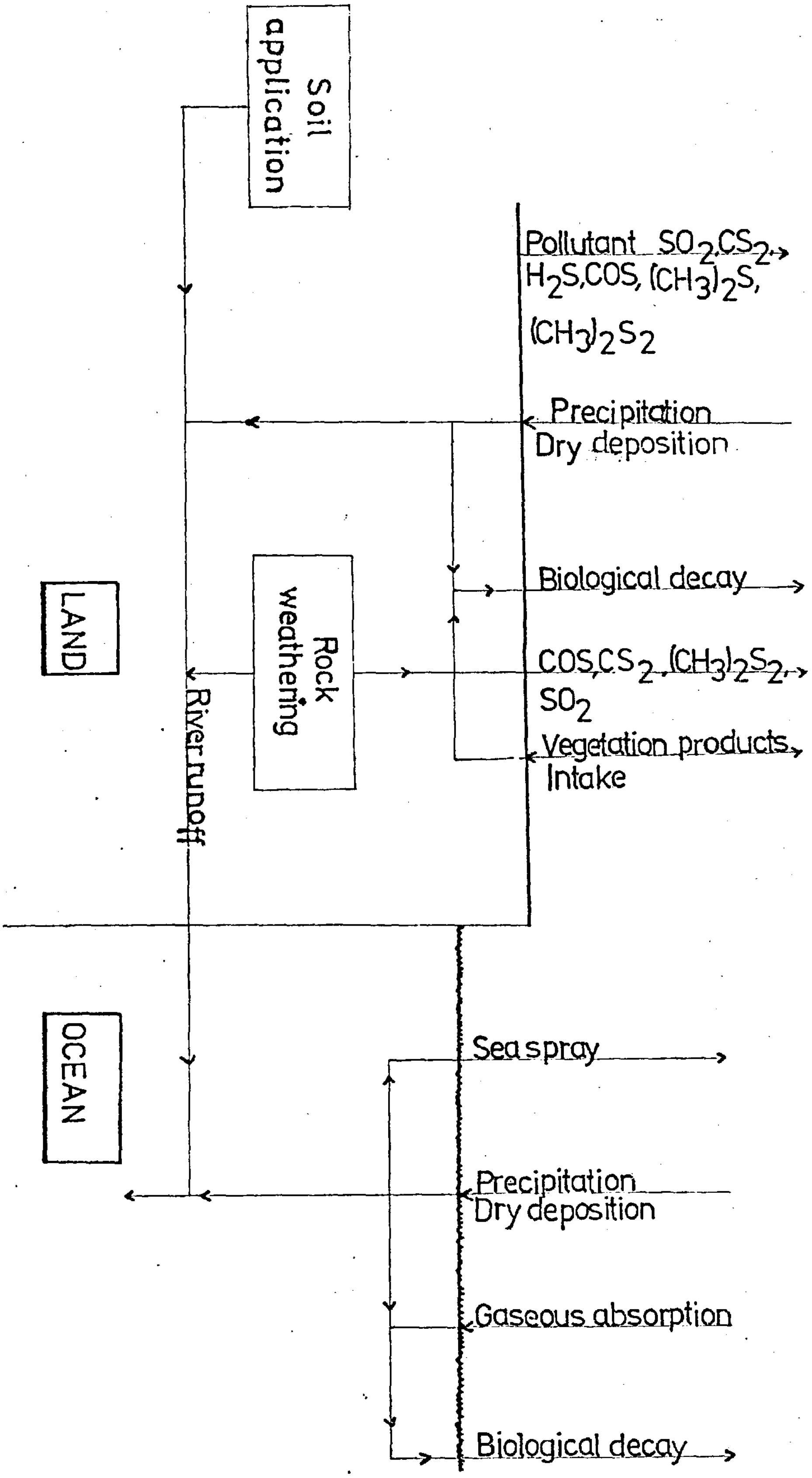

Fig. 2.2 The principal circulation of sulphur in Nature.

(Modified after Robinson and Robbins, 1970)

Table 2.6 Sulphur bacteria (Starkey, 1966; Postgate, 1968)

	Oxidizing				Reducing	
I	Colourless					
A	Thiobacillus		A	Desulphovibrio		
1	Thiobacillus	thioparus	1	"	desulphuricans
2	"	thioxidans	2	"	vulgaris
3	"	ferrooxidans	3	"	salexigens
4	"	novellus	4	"	gigas
5	"	neapolitanus	5	"	africanus
6	"	thermophlica			
			B	Desulphotomaculum	
B	Thiospirillum		1	"	nigrificans
C	Thiovulum		2	"	ruminis
D	Thiothrix		3	"	orientis
E	Beggiatoa				
F	Thioploca				
II	Green to purple coloured (photoautothrophs and lithoautotrophs)				
A	Chromatium				
B	Thiopedia				
C	Rhodothiospirillum				
D	Thiodendron				
E	Thiodyction				
F	Chlorobium				
G	Chloropseudomonas				

oxidation of sulphur dioxide and therefore are of fundamental importance in vapour geochemistry. Another application of the atmosphere in geochemistry is the vapour sampling of the soil atmosphere or the lower free atmosphere. A relationship between sulphur gases and concealed, weathering sulphide deposits has been reported (Rouse and Stevens, 1971); Shipulin et al, 1973 and many others). A more detailed description of sulphur forms in the atmosphere is presented in a later section of this thesis.

2.2.7 The anthroposphere

The concept of the anthroposphere was introduced by Pavlov owing to the fact that man becomes more and more important in his environment, causing changes in all geospheres and in the geochemical cycles of the elements (Rankama and Sahama, 1950). A worldwide contamination of the environment and pollution of the atmosphere is going on resulting in serious problems to living matter and property.

For the environmental geochemist problems appear when interpreting data from industrially affected regions. Gaseous sulphur compounds such as sulphur dioxide, methyl mercaptan etc; products from industrial activities are produced in large quantities. Not only mankind, but all living matter including vegetation are threatened. Sulphur dioxide may be further oxidized to sulphur trioxide and finally to sulphuric acid. The latter compound is precipitated together with rain, causing a decrease in pH levels.

Reference to anthropogenic sulphur vapours in the atmosphere is made elsewhere in this thesis.

2.2.8 The sulphur cycle with particular reference to sulphur vapours

2.2.8.1 Introduction

The sulphur cycle is very complex and not fully understood. It is impossible to study the sulphur cycle in its natural state owing to the anthropogenic contribution of sulphur gases.

The sulphur cycle in Nature is linked with volcanic activity, weathering of sulphides and dolomites/limestones and the removal of the sulphur from the oceans. The role of sulphur bacteria is considerable. A short description of microorganisms and their role in the transformation of sulphur follows below. Sulphur emissions, owing to industrial activities become more and more important in the sulphur cycle. It is generally believed that anthropogenic sulphur entering the atmosphere is half of the total (Weiss et al, 1971). The circulation of sulphur in Nature is shown by Fig. 2.2.

2.2.8.2 Microorganisms and their role in the transformation of sulphur

In the transformations of sulphur, the sulphur reducing and oxidizing bacteria are essential as well as other microorganisms. Chemical reactions without the aid of bacteria also take place. The role of bacteria in the production of sulphur gases of interest in exploration has been little investigated. Table 2.6 shows the most important genera and species.

Iron bacteria and certain yeasts which can deposit sulphur in their cytoplasm resemble sulphur-oxidizing bacteria. One bacterium belonging to this group is Ferrobacillus, which uses sulphur in its metabolic functions. Bloomfield (1972) suggests Ferrobacillus ferrooxidans to be a possible variant of Thiobacillus ferrooxidans.

Organic sulphur compounds reach the soil as residues of living matter and as products of microbial activity. Microorganisms are responsible mainly for the oxidation of organic sulphur compounds existing in soils (Freney, 1967). Products such as hydrogen sulphide and dimethyl disulphide, among other compounds may be formed by the decomposition of amino-acids and protein by various fungi such as Schizophyllum commune and Chlostridium tethamorphum (Frederick et al, 1957), which may interfere with gases evolved from oxidizing sulphides. Postgate (1968) claims that hydrogen sulphide, methylethiol and dimethyl sulphide are produced by bacterial activity on cystine under anaerobic conditions.

A description of the oxidation of sulphides, with and without the aid of bacteria is presented in Section 2.2.9.1.

2.2.8.3 Anthropogenic emission of sulphur-bearing air pollutants

The industrially produced sulphur gases are important to consider in vapour geochemistry, due to the fact that these are deposited sooner or later, over the land surfaces and may interfere with the naturally evolved sulphur products.

It has been mentioned elsewhere, that the anthropogenic emission of sulphur gases becomes more and more important owing to their influence on the environment. The circulation of sulphur in Nature, in and between the geospheres, is complicated and extensive. There is a continuous transport to and from the different reservoirs and it is therefore of fundamental importance to find out the influence of man-made contribution of sulphur, mainly in the form of sulphur dioxide pollutant. A possible way to track the origin of sulphur compounds is with the aid of isotopes. It has been reported that sulphur dioxide is mainly of anthropogenic origin, while hydrogen sulphide (if measurable) seems to be a natural product (Junge, 1960). Hales et al (1974) mention hydrogen sulphide and methyl mercaptan to be of natural origin. The oxidation of hydrogen sulphide and methyl mercaptan takes place rapidly, resulting in the formation of sulphur dioxide:

$$H_2S + O_3 \rightarrow SO_2 + H_2O$$

Georgii (1970) reported that sulphur dioxide produced by industrial activities dominates in the lower part of the atmosphere but decreased considerably with increasing altitude. Robinson and Robbins (1970) claim that one third of all sulphur reaching the atmosphere, originates from industrial activities and occurs mainly as sulphur dioxide. 93 percent of pollutant emissions occur north of the equator. In the world, more than two-thirds of the volume of natural and pollutant sulphur emissions occur in the northern hemisphere.

Sulphur dioxide and other sulphur-containing pollutants may be removed from the atmosphere in three ways: (1) by precipitation, (2) by oxidation resulting in particulate matter such as aitken nuclei (10^{-7} - 10^{-5} cm), larger sulphate particles and H_2SO_4 - containing particles and (3) by direct interaction of the gas molecules with the lower boundary of the atmosphere (dry deposition).

In the presence of sunlight, sulphur dioxide can be oxidized to sulphur trioxide, which is subsequently converted to sulphuric acid if water is present. The first reaction is photochemical and the other is catalytic. The relative importance of these two processes in the atmosphere is difficult to determine. It is likely that photochemical oxidation predominates in dry areas, while the catalytic oxidation predominates in areas with sufficient clouds, fog and rain formation. In alkaline or neutral water vapour, sulphur dioxide is oxidized to sulphate which is adsorbed by particles and rain water in the atmosphere. The dispersion of sulphur in the atmosphere is difficult to estimate. Georgii (1970) claims that sulphur dioxide is not transported far from its sources, owing to short residence time of sulphur dioxide, while Smith and Jeffrey (1975) report that sulphur dioxide can move considerable distances in the atmosphere before deposition. They mention that Scandinavian areas may be affected of sulphur dioxide, originating from Great Britain. Close to industrial areas, the concentration of sulphur dioxide may increase and become several times higher than the average background concentration (Barringer, 1966). Bremner and Banwart (1976) have reported alkyl sulphides, carbonyl sulphide and carbon disulphide as pollutants in the atmosphere.

2.2.8.4 Sulphur forms in the atmosphere

In the extensive circulation of sulphur, from one form to another in the sulphur cycle, the atmosphere is a widely important and necessary medium. Present results on forms and concentrations of sulphur compounds in this reservoir are questionable, owing to the lack of measurements in unpolluted regions but a few and sensitive and reliable analytical methods.

The atmosphere is a mixture reservoir of natural and anthropogenic sulphur emissions. In Section 2.2.9, all natural sources of sulphur vapours are described as well as the products. Sulphur dioxide is the main pollutant. Hydrogen sulphide, alkyl sulphides, carbon disulphide and carbonyl sulphide have been reported to be air pollutants in some areas by Robinson and Robbins (1970) and Bremner and Banwart (1976). It has been found that the concentration of hydrogen sulphide in the atmosphere is somewhat constant and unaffected by the origin and history of the air masses, while the concentration of sulphur dioxide differs owing to meteorological and environmental factors. In polluted regions, concentrations of sulphur dioxide in the range 0.2 - 2 ppm have been reported by Smith et al (1961) and Barringer (1966). Eriksson (1970) reports an average atmospheric concentration of 0.1 ppb of sulphur dioxide, which is about the same concentration as Robinson and Robbins (1970) found for the troposphere. Estimations of atmospheric hydrogen sulphide are few. Robinson and Robbins (1970) claim that the average tropospheric concentration is 0.2 ppb. This compound is believed to be rapidly oxidized to sulphur dioxide by ozone. No information has been found concerning the atmospheric concentrations of organic sulphur gases. Lovelock and Maggs (1972), Hales et al (1974), Kadota and Ishida (1972) and Rasmussen (1974) suggest that alkyl sulphides and methyl mercaptan are released from decaying living matter. Volcanoes, springs etc. also deliver sulphur gases such as hydrogen sulphide and sulphur dioxide to the atmosphere.

2.2.9 Important natural sources of sulphur vapours

In Section 2.2.6 the essential sources of volatile sulphur compounds were given. The anthropogenic contribution has been treated in Section 2.2.8.3. In the following pages oxidation, bacterial and volcanic activities and their products will be considered.

2.2.9.1 Oxidation

It has been reported in the literature that sulphur dioxide and other volatile sulphur compounds are derived from oxidising sulphide deposits (Shipulin et al, 1973; Kahma et al, 1975; Glebovskaya, 1969; Rouse and Stevens, 1971). As all initial work of the present research was based on these results it is necessary to take a closer look on the processes involved.

Igneous rocks, formed in primary environments are not stable under supergene conditions owing to new physical-meteorological conditions. The weathering of rocks may be divided into three types: (1) physical weathering, (2) chemical weathering and (3) biological weathering. The rate of weathering is controlled by factors such as climate, topography, relief and resistance of rock-forming minerals to alteration. The oxidation of sulphide ore deposits depends on pressure and temperature, pH and Eh and the position of the ground-water table. Besides, the presence of a population of oxidizing microorganisms is important in the oxidation processes taking place on the surface of the Earth.

Ginzburg (1960) says that the oxidation of sulphides is most developed in regions with warm and humid climate. Areas with alternating daily or seasonal, wet and dry periods or where the ground-water table fluctuates are frequently subjected to intensive and deep rates of oxidation. The acidity of the environment plays an important role in its influence on the microorganisms taking part in the oxidation processes. It has been shown that bacteria are most active under conditions of a low pH, a temperature of about 30°C and the necessary presence of oxygen, sulphur iron and nutrients. The depth of oxidation in tectonically stable areas extends to the water level. In arid regions, where the water level is most likely to be deep, the oxidation zone may extend several hundred meters below the surface, while in humid areas the oxidation zone normally extends just to no more than a few meters. The oxidation of sulphides may be divided into subsurface oxidation and surface oxidation. The former is mostly chemical and occurs in an environment, which is not in contact with the atmosphere. The latter, on the other hand, occurs under conditions when the atmosphere is in intimitate contact with the deposit and can be both chemical and microbiological. The non-biological surface reactions are insignificant as compared with those carried out by bacteria. Starkey (1966) mentioned that the surface oxidation is mainly due to microorganisms of the genera Thiobacillus and Ferrobacillus.

When sulphides oxidize, sulphate and sulphuric acid are formed. The latter attacks sulphides and hydrogen sulphide is formed. Some of the sulphate is metabolized by microorganisms and plants, while the rest is leached away in humid regions. In areas of arid and semi-arid climate, the sulphates precipitate in form of gypsum and other minerals. As pyrite is the most common sulphide mineral in a wide range of deposits, soils and environments some reactions of this compound is presented below. The formation of pyrite in soils may be caused by hydrogen sulphide (possible derivation-product from the decomposition of organic matter) and iron hydrate or by hydrogen sulphide and iron sulphide.

The following reactions are taken from Harmsen (1954) and Starkey (1966).

$$2Fe(OH)_3 + 3H_2S \rightarrow FeS + S + 6H_2O$$
$$FeS + S \rightarrow FeS_2$$

or

$$2FeS + 2H_2S + O_2 \rightarrow 2FeS_2 + 2H_2O$$
$$FeS_2 + H_2O + {}^7/_2O_2 \rightarrow FeSO_4 + H_2SO_4$$
$$2FeSO_4 + {}^1/_2O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O$$
$$Fe_2(SO_4)_3 + FeS_2 \rightarrow 3FeSO_4 + 2S$$

Sulphur formed in the last reaction may be oxidized to sulphur dioxide.

In the literature, information has been presented about the possible emission of hydrogen sulphide, sulphur dioxide and carbonyl sulphide from oxidizing sulphur deposits. The origin of these volatiles has not been explained. It is possible that bacterial or chemical processes on sulphides cause the formation, but it is also possible that the derived products are caused by microbiological decomposition of organic matter in soil.

In the following section the bacteriogenic formation of sulphur vapours will be considered.

2.2.9.2 Bacteriogenic origin

Microorganisms, except bacteria, such as fungi and algae also take part in the transformation of sulphur, but are of a minor importance as compared with the bacteria.

The role of bacteria in the oxidation of ore deposits was briefly considered in a previous section.

Bacteria are very important in oxidation-reduction processes of sulphur and its compounds, transforming sulphur from one form to another (Starkey, 1966). In vapour geochemistry, it is of interest that volatile sulphur compounds are formed in these processes. In other sections of this thesis, descriptions of products from decaying matter have been presented. The main constituents reported are hydrogen sulphide, dimethyl sulphide, dimethyl disulphide, methyl mercaptan, carbonyl sulphide and carbon disulphide. Few suggestions have been presented about bacterially derived volatile sulphur compounds from sulphide ores. Shipulin et al (1973) mention hydrogen sulphide, which subsequently is oxidized to sulphur dioxide.

Rasmussen (1974) analysed the headspace* over non-organic sulphur media ($MgSO_4$) and found that dimethyl disulphide was produced by microbes and that dimethyl disulphide and dimethyl sulphide and other unidentified sulphur gases were produced by bacteria grown on organic material.

The sulphate-reducing bacteria are found in a wide variety of environments. They exist in soil and waters, in muds, in sulphur springs and in oil pools. Their presence is revealed by a dark colour of the soil and a smell of sulphide. If they accumulate in large numbers, precipitation of metal sulphides may take place. The soil changes to yellow, red or orange when oxidized.

2.2.9.3 Volcanic emanations

Nearly all volcanoes give off hydrogen sulphide. Often sulphur dioxide, sulphur trioxide and carbonyl sulphide are emitted. The first two gases can be oxidation products of hydrogen sulphide and carbonyl sulphide can have been formed by a reaction between carbon dioxide and a sulphur gas.

Almost all data on the composition of volcanic gases comes from fumaroles. A world-wide similarity of the emissions from fumaroles exists. It seems that water vapour is the most dominant gas, followed by carbon gases (CO_2, COS etc.) and sulphur gases on the third place.

2.2.9.4 Other sources

Hydrogen sulphide and its oxidation products have

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*Headspace is defined as the gaseous atmosphere over a sample in a closed system.

also been found in springs, salt deposits, oil and gas pools etc.. Many times, hydrogen sulphide is escaping from seeps close to these formations, suggesting another possibility for the use of sulphur vapour geochemistry in exploration.

2.2.10 Factors concerned with form, dispersion and concentration of sulphur vapours in soil

Oxidation of sulphides and putrefaction of organic matter may cause an emission of various volatile sulphur compounds. For the exploration geologist, the former is of particular interest. Many factors are of importance when considering form, dispersion and concentration of these compounds.

The form of compounds evolved depends on parameters such as: (1) environment (aerobic or anaerobic), (2) geology (type of rock and mineralization, (3) chemical or microbiological activities and (4) meteorological factors (temperature and temperature changes, barometric pressure, wind velocity and precipitation). Rouse and Stevens (1971) and Shipulin et al (1973) have found that different rocks and sulphide mineralizations emit a various amount of sulphur vapours. It is also believed that the emission may vary during the day and night, being most intensive during daytime, when the deposits are subjected directly to the action of sunlight. Fluctuation of temperature, groundwater level etc., owing to seasonal or periodical changes, also affects the production of gases. Type of mineralization and population of microorganisms determine the formation of sulphur gases. Sulphates e.g. are reduced by bacteria under formation of hydrogen sulphide, while sulphides are oxidized, during which process sulphur dioxide and carbonyl sulphide may be evolved. The dispersion of the volatiles is affected by factors such as (1) structural geology, (2) permeability of overburden, (3) soil moisture content, (4) microorganisms and plants and (5) further transformations of the sulphur compounds in the cycle of sulphur.

Ovchinnikov et al (1972), Ernst (1968) and Headlee (1962) report that fractures and cracks act as pathways for gases derived from subsurface environments on their way to the atmosphere. Terraglio and Manganelli (1966) have examined the influence of soil moisture on adsorption of sulphur dioxide in soils. They found that an increasing moisture content results in an increasing adsorption capability of the soil. Other parameters such as the pH of the soil, soil structure, mineral or organic content, porosity and ion exchange capacity may also be of importance in the dispersion, since these factors affect microorganisms and plants.

The concentration of sulphur vapours in soil depends mainly on the following factors: (1) type of rock, (2) adsorption capability of the soil, (3) meteorological factors and (4) distance from the ore deposit. Under near-surface conditions the concentration of gases are affected by meteorological variables such as precipitation, which causes dilution or concentration of sulphur gases in soil moisture and changes in barometric pressure, which affects the direction of the gasflow in the surface layer. The soil will either be degassed or enriched by gases entering the soil from the atmosphere.

2.2.10.1 Geochemical haloes

As the surficial pattern formed by sulphur gases, generated from concealed, oxidizing sulphide-bearing deposits and the relationship between gaseous sulphur compounds and sulphide minerals are not known, geochemical haloes in general are briefly described below.

Geochemical haloes are often formed above or beside ore deposits. There are two types: (1) primary (syngenetic) which are associated with endogeneous and exogeneous mineralizations and (2) secondary, which have developed under exogeneous conditions depending on subsurface chemical reactions and degassing of the Earth. These can be further subdivided into the following types: mechanical, saline, biogeochemical, water and gas. Primary and secondary haloes vary widely in their natural appearance. Haloes in the supergene zone are probably of mixed primary and secondary origin. Above gas and oil deposits, there are so called intrusion haloes, which consist of hydrocarbons. Factors affecting the morphology and dimensions of geochemical haloes, associated with ore deposits, are listed below:

(1) Structure (including tectonic features such as faults, fractures and contact zones between ore and host rock),

(2) Lithological-petrological composition of the ore deposit and host rock,

(3) Mineralogical-chemical composition of the ore deposit and host rock,

(4) The genesis of ore formation,

(5) Porosity and permeability of the host rock and overburden.

Primary haloes related to exogeneous mineralizations are also affected by facies changes. Endogeneous haloes are often irregular and spread upwards, seldom in the lateral direction. Bakhtin (1972) describes the magnitude of certain aureoles in Russia and suggests that above pyrite deposits with a steep dip, there are endogeneous haloes with a vertical extent of 500 - 2000 m. He further states that the width of endogeneous haloes above polymetallic deposits in Caucasus may be 30 - 50 times greater than the thickness of the ore bodies. Secondary haloes generally have a larger areal extent than primary haloes. Secondary haloes are affected by erosion.

Elements with an affinity for sulphur form larger dispersion aureoles than those with an affinity for oxygen (Kreiter, 1968).

Horizontal and vertical zonation in haloes exist. The former type is signified of a decrease in concentration with an increasing distance from the ore body. Vertical zonation is affected by structure and temperature conditions. Increasing distance from the mineralization leads to a lower concentration.

It is important in understanding the dispersion and kind of gases connected with ore deposits to know the possible sources of the origin of the gases. Elinson et al (1970) summarize following origin for gases:

(1) Residual gases which were originally present in rocks,

(2) Gases introduced with the hydrothermal solutions,

(3) Gases formed during metamorphic and metasomatic alterations,

(4) Gases from great depths,

(5) Gases derived from oxidizing ore bodies.

Gas haloes above ore deposits are formed in the zone of endogeneous haloes and near the surface. Mobile gaseous aureoles can be grouped into different types according to their genesis as: (1) those of polygenetic origin, formed at great depths and related to tectonic zones and (2) those derived from oxidizing ores.

2.2.10.2 The migration of gases

Generated gases migrate upwards, either directly or in steps, owing to dissolution and evaporation processes. Because of pressure and concentration gradients, lateral movement exists. Stegena (1961) and Headlee (1962) mention the vertical movement to be the most significant.

There are two mechanisms responsible for the migration of gases or for the exchange of gases between the soil and atmosphere. They are massflow (effusion), which depends on differences in total pressure and diffusion, which depends on differences in concentration.

In any transport, three variables, a flux F, a conductivity K and a potential gradient G, measured in the direction of flow, are related according to Fick's law by the equation (Currie, 1970)

$$F = K \times G$$

The exchange of gases between the soil and atmosphere is affected mainly by diffusion (follows Fick's law above) and meteorological factors such as changes in temperature and atmospheric pressure, wind and precipitation. Kohnke (1968) and Currie (1970) also mention massflow as a mechanism, acting in a role of the removal of soil air. Blake and Page (1948) state that diffusion is the most important of the two mechanisms as well as the two authors previously mentioned. Gaseous diffusion in a soil is controlled by soil structure and soil moisture. The rate of diffusion through soils is mainly determined by the total volume and not the size of the pores. Diffusion takes place continuously until the components of any gas-filled space are mixed and in a state of chemical and physical equilibrium.

Changes in barometric pressure and temperature, wind and soil moisture content will affect the massflow of soil gases. The alterations in soil air, depending on massflow are very small, since the result of action of the determining factors are insignificant.

Groundwater is another medium in which gas transportation may occur. Hydrogen sulphide and sulphur dioxide are very soluble. When the pressure declines, the dissolved gases may be released from the water by evaporation. The influence of groundwater on sulphur gases is significant in those cases when the mineralization is below the groundwater table.

2.2.10.3 Sorption of sulphur gases by soils

Little information has been found in the literature about sorption of sulphur gases by soils. Most papers reviewed deal with the sorption of sulphur air pollutants, of which sulphur dioxide is the most important, by the lower boundary of the atmosphere. This is important in sulphur vapour geochemistry, since the fate of sulphur pollutants in the atmosphere is little known. Sulphur gases, removed from the atmosphere by soil and water surfaces, undergo further transformations, chemical and microbial, and become more and more important in the sulphur cycle. It is unknown if the deposited gases remain in the top layer of the soil or if they penetrate the soils to a considerable depth on account of their solubility in water and hence transport with this medium. In sulphur vapour geochemical exploration for concealed sulphide ore deposits, the soil atmosphere is often sampled at a depth of 30 - 100 cm and might be affected by the atmospheric sulphur-containing gaseous constituents. The fate of atmospheric sulphur-bearing pollutants and the sorption of sulphur gases by wet and dry soils are briefly discussed below.

Sulphur gases such as sulphur dioxide may be removed from the atmosphere in rain, by oxidation to particulate material or by direct interaction of the gas molecules with the land and water surfaces. Many parameters affect the deposition. The most important are meteorological factors such as wind velocity, physiochemical properties like pH, type of vegetation, moisture content and effective surface area for land surfaces (Payrissat and Beilke, 1975; Terraglio and

Manganelli, 1966; Garland et al, 1974). Few workers have contributed with information on sorption of sulphur gases, except sulphur dioxide, by soils. Smith et al (1973) describe sorption of sulphur dioxide, hydrogen sulphide and methyl mercaptan. They found that the moisture content is important for the removal of particularly sulphur dioxide and that dry soils sorb hydrogen sulphide and methyl mercaptan more rapidly than wet (Fig. 2.1). Bremner and Banwart (1976) have investigated evolution and sorption of sulphur gases such as carbon disulphide, carbonyl sulphide, hydrogen sulphide, sulphur dioxide, methyl mercaptan, sulphur hexafluoride, dimethyl sulphide and dimethyl disulphide. Sulphur hexafluoride was included on account of its inert properties and its suitability as a tracer gas for air pollution. They found that air-dry and moist soils have the capacity to sorb dimethyl sulphide, dimethyl disulphide, carbonyl sulphide and carbon disulphide but not sulphur hexafluoride. Dimethyl disulphide, dimethyl sulphide, carbonyl sulphide and carbon disulphide were sorbed in larger amounts by wet soils. Hydrogen sulphide, sulphur dioxide and methyl mercaptan are sorbed more rapidly than all the others. Carbonyl sulphide is more easily adsorbed by wet soils than alkyl sulphides and carbon disulphide. Smith et al (1973) found that sulphur dioxide is more rapidly sorbed than hydrogen sulphide and methyl mercaptan by wet and dry soils. Bremner and Banwart (1976) found that the microbacterial population of a wet soil is the main factor for the sorption of alkyl sulphides, carbonyl sulphide and carbon disulphide. Sorption of the gases investigated by Bremner and Banwart

(1976) is illustrated in Fig. 2.3.

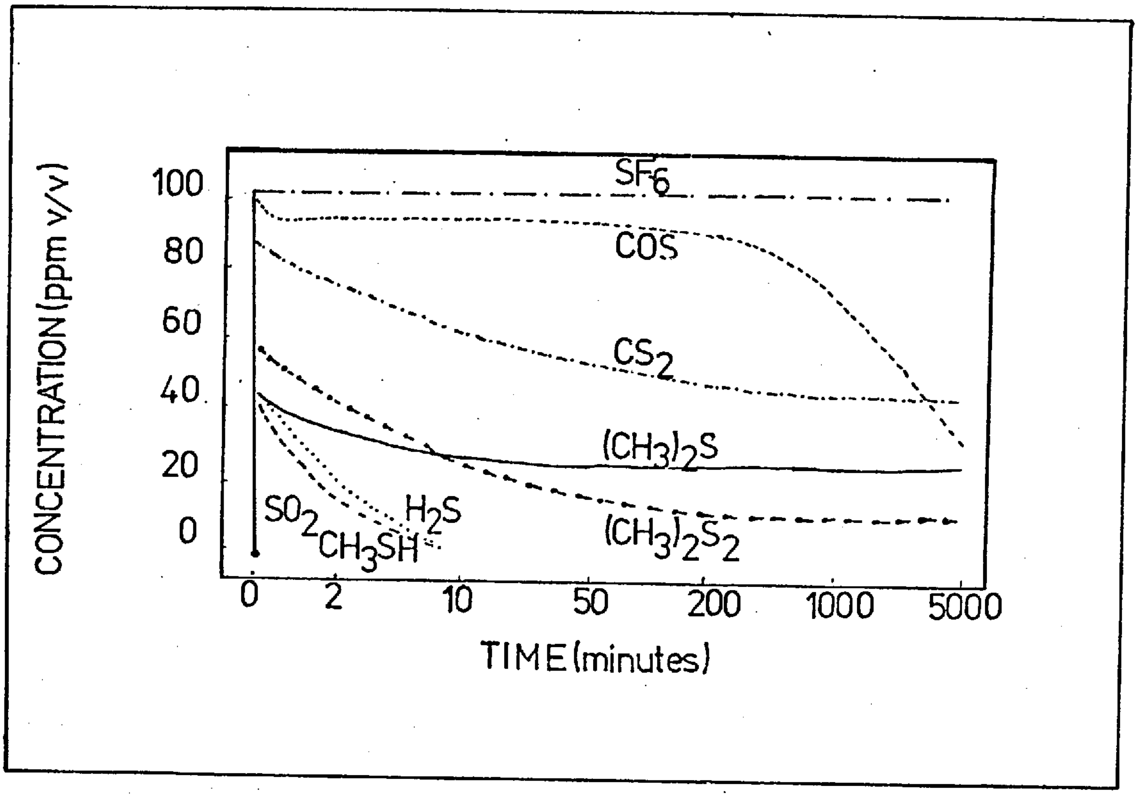

Fig. 2.3 Sorption of different sulphur gases by air-dry soil from air initially containing 100 ppm (v/v) of these gases. (Bremner and Banwart, 1976)

CHAPTER 3

SPECIFIC NON-INSTRUMENTAL ANALYTICAL METHODS FOR SULPHUR DIOXIDE AND HYDROGEN SULPHIDE IN SOIL GAS

3.1 Introduction

Based on the positive claims by previous workers (Chap. 1) that sulphur dioxide and hydrogen sulphide in soil gas could be used in exploration for detecting sulphide-bearing mineralization, an extensive literature review on techniques used in the detection of these two compounds was carried out.

Until recently, mainly wet-chemical methods have been used in the analysis of sulphur dioxide and hydrogen sulphide. Latterly, the need for more rapid and sensitive techniques has become necessary because of the extremely low concentrations and environmental contamination.

For the analysis of sulphur dioxide in the parts per billion (ppb) concentration range, Peters (1973) used a method, developed by West and Gaeke (1956), and could detect sulphur dioxide in soil gas above concealed sulphides in Canada. Of the numerous analytical methods available for sulphur dioxide, the West-Gaeke colorimetric method was selected for the present research in sulphur vapour geochemistry owing to its high sensitivity, simplicity and low cost.

Many methods are available for the detection of hydrogen sulphide. Two methods, one colorimetric and the other using a sulphide-ion selective electrode, were tested for their proclaimed high sensitivities.

In the following sections a presentation of the selected analytical methods is given, followed by experimental work utilizing the methods selected and the results obtained.

3.2 Previous Work

3.2.1 Application of the West-Gaeke method in the analysis of sulphur dioxide

West and Gaeke (1956) developed a wet-chemical method for the analysis of sulphur dioxide, that came to be widely used in air pollution control. Many modifications have thereafter been made in attempts to minimize errors and lack of reproducibility.

The detection limit of the original method was claimed to be 5 ppb for a 38.2 ℓ sample (West and Gaeke, 1956; Trieff et al, 1968). The procedure of the original method was:

> An absorbing solution of 0.1 M sodium tetrachloromercurate (II) ($Na_2HgC\ell_4$) traps sulphur dioxide as dichlorosulphitomercurate (II) ($Hg(SO_3)_2C\ell_2$) When acid-bleached pararosaniline dye and formaldehyde are added, the red-purple-violet pararosaniline methyl sulphonic acid complex is formed. The optical density of the coloured solution is determined spectrophotometrically at a wavelength of 5600 Å. The intensity of the colour is directly proportional to the concentration of sulphur dioxide.

Scaringelli et al (1967) investigated the relationship between the concentration of the tetrachloromercurate solution (TCM) and the absorbance of sulphur dioxide. They found that concentrations higher than 0.04 M restrain colour formation of the disulphito-mercurate (II) complex and claim that the TCM solution may be diluted 10 - 100 times without any loss in absorbing efficiency (Fig. 3.1).

West and Gaeke (1956) carried out a test comprising the oxidation of sulphur dioxide absorbed in TCM. They found that the sulphur dioxide was very stable and that no oxidation took place (Fig. 3.2). Reiszner and West (1973) claim that not even permanganate oxidizes the dichlorosulphitomercurate complex

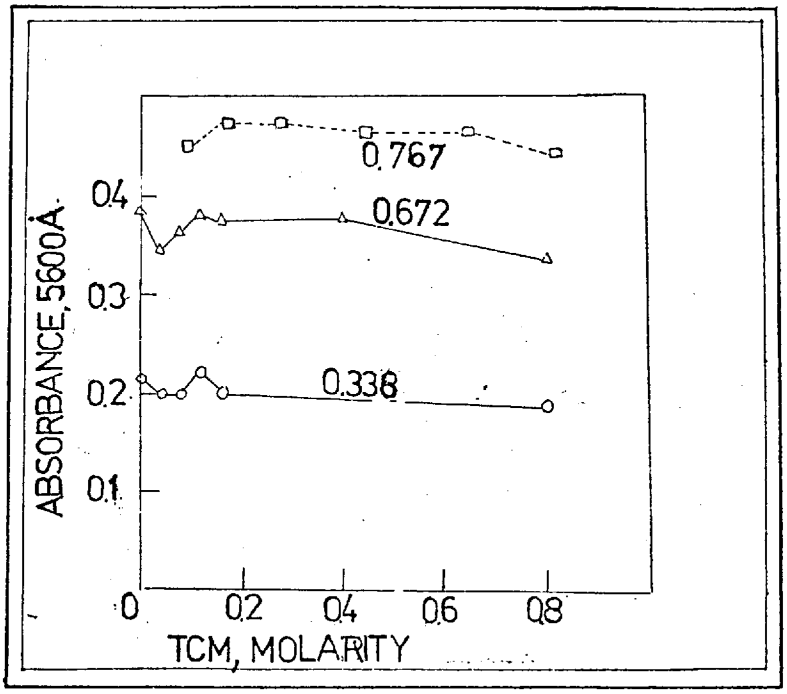

Fig. 3.1 Absorbance at various concentrations of tetrachloromercurate (TCM) for three concentrations of sulphur dioxide (μg/mℓ). (Scaringelli et al, 1967)

(II). The stability of the complex with time and light was investigated by Scaringelli et al (1967). Their tests showed that a significant loss of sulphur dioxide took place in solutions exposed to intensive light. Reiszner and West (1973) report a rapid decay of dichlorosulphitomercurate in solutions exposed to the sun. The complex was found to be stable for a long time at low temperatures, while a loss of sulphur dioxide could be observed at higher temperatures (Fig. 3.3).

The pararosaniline dye has been found to contain impurities by many users and Scaringelli et al (1967) recommended thorough cleaning before use.

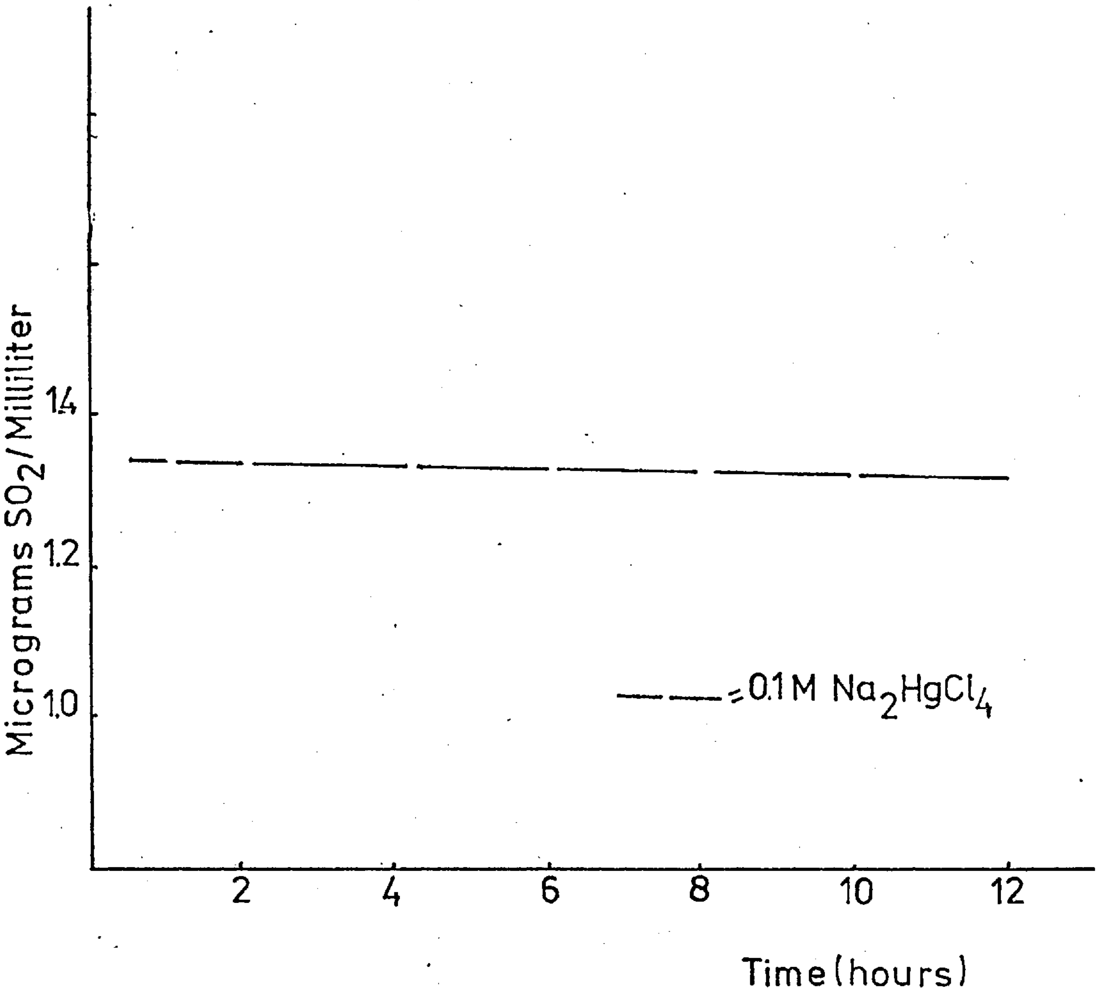

Fig. 3.2 Rate of oxidation of sulphur dioxide absorbed in sodium tetrachloromercurate (TCM). (West and Gaeke, (1956)

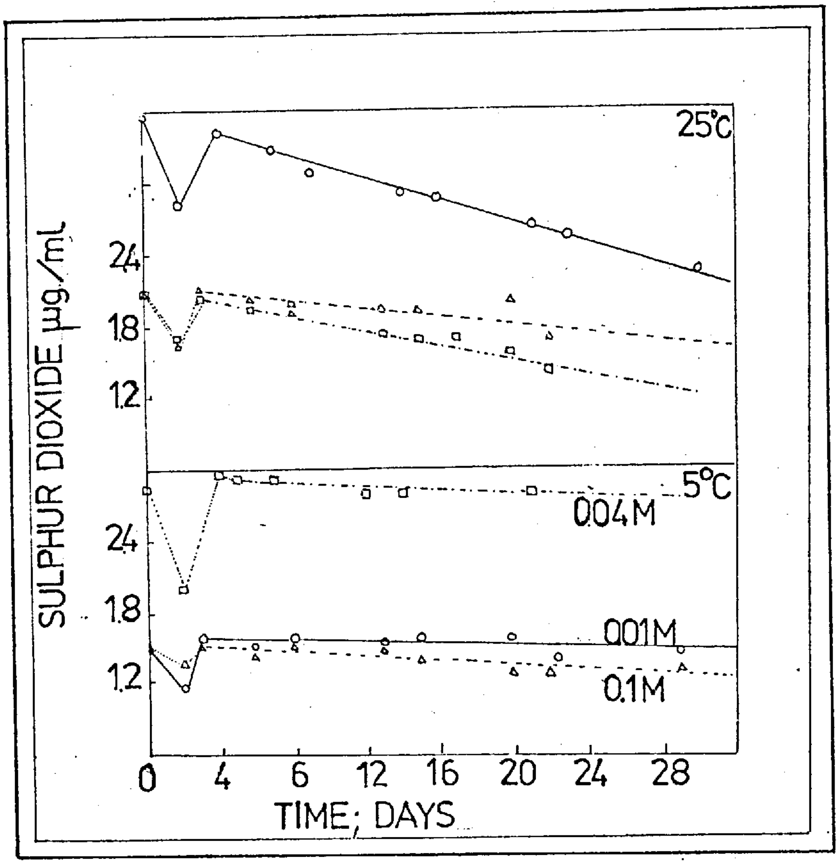

Fig. 3.3 Stability of dichlorosulphitomercurate solutions with time. (Scaringelli et al, 1967)

Complete colour development is achieved after 20 - 30 minutes according to West and Gaeke (1956). Trieff et al (1968) report a tendency of variability of the colour development from sample to sample. Scaringelli et al (1967) investigated relations between temperatures and colour variations. Fig. 3.4 shows that the fading of the colour is most intense at high temperatures.

The most serious interferences reported are nitrogen dioxide and heavy metals. The former can be eliminated by the addition of sulphamic acid directly after the sampling (Scaringelli et al, 1967). The influence of heavy metals may be eliminated by the addition of EDTA or phosphoric acid.

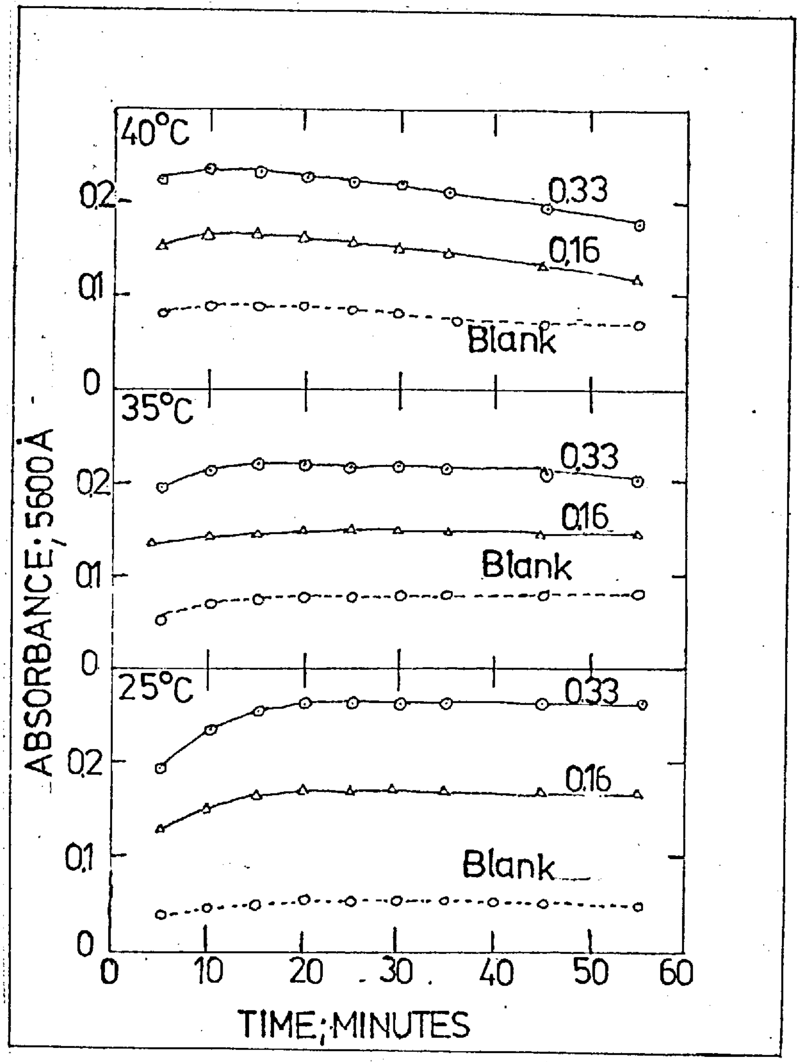

Fig. 3.4 Absorbances versus time at specified temperatures. (Scaringelli et al, 1967)

3.2.2 Application of the methylene-blue method in the analysis of hydrogen sulphide

For the detection and estimation of hydrogen sulphide in ambient air, Jacobs (1957, 1959) recommends the methylene-blue colorimetric method. The original procedure of the methylene-blue method is as follows:

> An alkaline solution of cadmium hydroxide acts as an absorbent of hydrogen sulphide. The gas is trapped as cadmium sulphide and precipitates. The hydrogen sulphide is released by acidification with p-aminodimethylaniline (Fig. 3.5). Ferric chloride, hydrogen sulphide and p-aminodimethylaniline produce methylene blue (Fig. 3.6). The absorbance of the colour is measured spectrophotometrically at 6700 A. The intensity of the colour is directly proportional to the amount of cadmium sulphide and hence of the concentration of hydrogen sulphide.
>
> $$CdSO_4 + 2NaOH \rightarrow Cd(OH)_2 + Na_2SO_4$$
> (alkaline)
>
> $$Cd(OH)_2 + H_2S \rightarrow CdS + 2H_2O$$
>
> $$CdS + H_2SO_4 \rightarrow CdSO_4 + H_2S$$
>
> (The amin-acid stock solution is made of 12 g p-aminodimethylaniline, 50 ml concentrated sulphuric acid and 30 ml distilled water).

Jacobs et al (1957) and Jacobs (1959) describe problems with the oxidation of hydrogen sulphide. Bamesberger and Adams (1969) compared concentrations recovered in the alkaline cadmium hydroxide absorbing solution with known generated concentrations. During a two-hour sampling period, up to

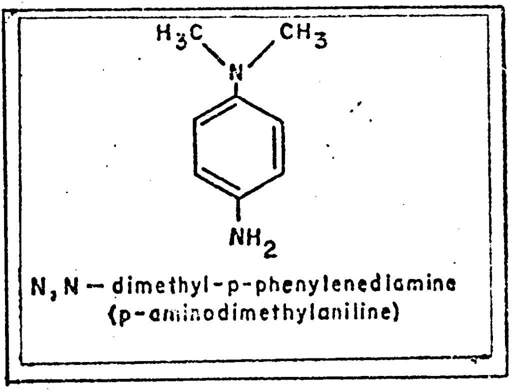

Fig. 3.5 p-aminodimethylaniline (Jacobs, 1959)

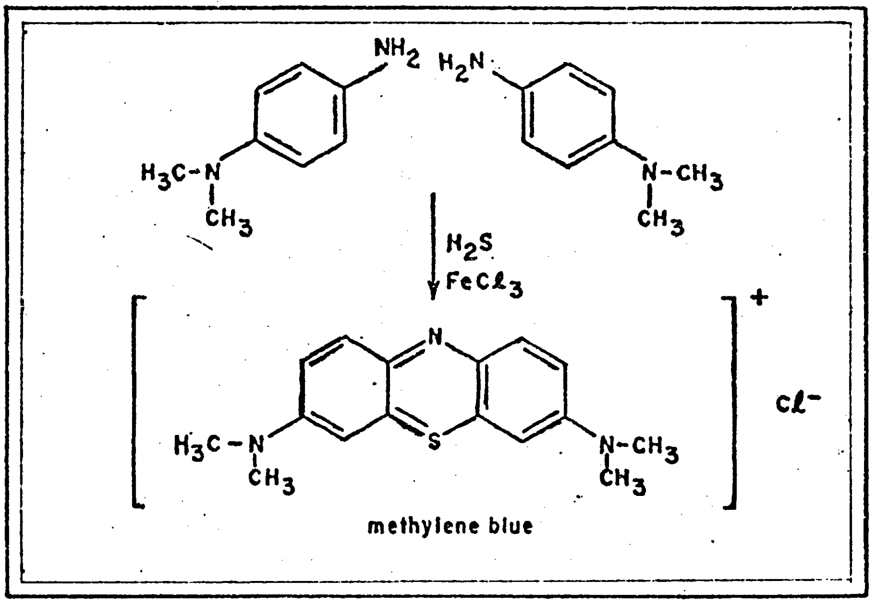

Fig. 3.6 Formation of methylene blue (Fe Cl_3 acts as an oxidant in the reaction). (Jacobs, 1959)

80% of the hydrogen sulphide was lost. An investigation of factors such as pH, oxygen, aspiration and light showed that the major loss was caused by exposure to light (Fig. 3.7). The photodecomposition of the cadmium sulphide precipitate could be inhibited by the addition of an antioxidant, arabinogalactan, and hence improve the recovery of hydrogen sulphide. The effects of aspiration and pH are shown in Fig. 3.8.

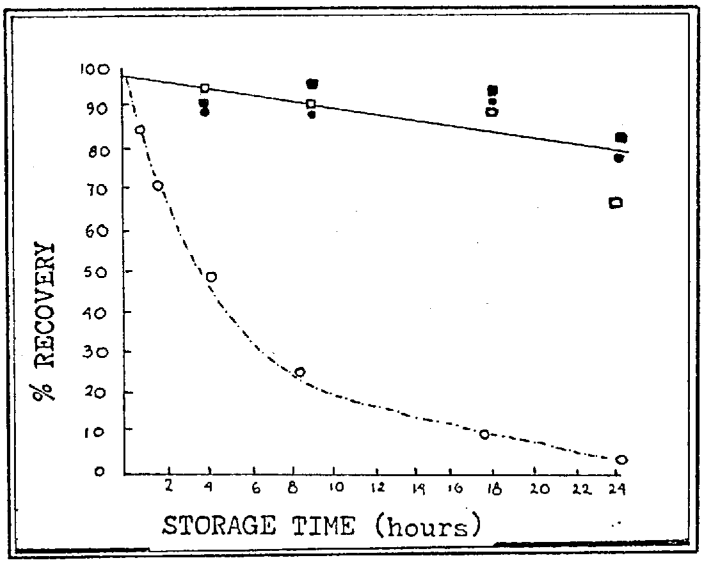

Fig. 3.7 Effect of light on cadmium sulphide in a cadmium hydroxide suspension. (Bamesberger and Adams, 1969)

LEGEND

■ Anti-oxidant, dark

□ Anti-oxidant, light

● No additive, dark

○ No additive, light

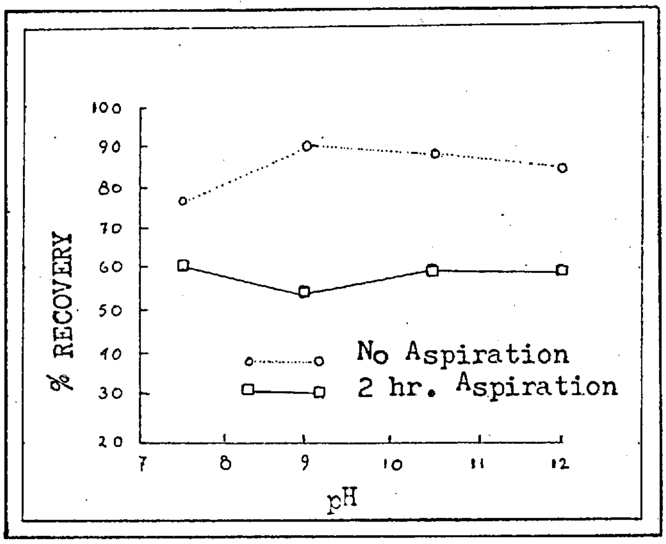

Fig. 3.8 Effect on pH on loss of sulphide from a cadmium hydroxide solution in the dark. (Bamesberger and Adams, 1969)

In Table 3.1, the effects of oxygen and nitrogen are compared with the role of photodecomposition of cadmium sulphide.

Table 3.1 Oxidation versus photodecomposition for hydrogen sulphide

Dilution gas	Light exposure (hours)	μg H_2S/sample	H_2S recovered (%)
N_2	0	11.78	81.8
O_2	0	11.52	80.0
Air	0	11.43	79.4
	2	8.96	62.2
	24	0.42	2.9

Jacobs et al (1957) carried out a test comparing the efficiency of the absorbing solution by connecting three scrublers with cadmium hydroxide and a hydrogen sulphide generator in series. The first washer trapped the atmospheric hydrogen sulphide. Thereafter, the purified airstream passed through the hydrogen sulphide-generating container, continuing into the two remaining two washers. The first of these was found to absorb at least 90% of the hydrogen sulphide generated.

3.2.3 Analysis of hydrogen sulphide with a sulphide-ion selective electrode

In recent years a range of electrodes capable of responding to a particular ion has been developed. They are very selective for a particular ion such as F^-, S^{2-}, K^+, Na^+ etc.

The application of a sulphide-ion selective electrode in the analysis of hydrogen sulphide has become common owing to (1) simplicity, (2) freedom of interferences (3) high sensitivity and selectivity and (4) direct determination of the sulphide concentration or activity in solution. The application of this method makes possible the measurement of hydrogen sulphide below the ppb level in solution. The total sulphide ion activity in a solution can be measured as well as the free hydrogen sulphide. Depending on pH, sulphur of oxidation number two can be present as sulphide (S^{2-}), hydrosulphide (HS^-) or hydrogen sulphide (H_2S) in a solution. An increase of sulphide (S^{2-}) is observed with rising pH.

The specific sulphide-ion electrode consists of a solid homogeneous high-purity silver sulphide membrane separating a dilute silver nitrate internal reference solution and a silver wire (Fig. 3.9). The metallic silver cannot come into contact with the sample. The possibility of measuring oxidation-reduction potentials is thus eliminated, leading to improved specificity and performance. The membrane is used as a connector that allows only silver ions to pass between the sample solution and the reference solution which is kept at a constant silver ion concentration. Electrical conductivity is formed between the sample solution and the internal reference solution, which depends on the activity of the silver ion in the sample solution (Hseu and Rechnitz, 1968). As the sulphide-ion membrane electrode exhibits Nernstian behaviour, the activity of the silver ion can be expressed by Nernst's equation as below (Müller et al, 1969):

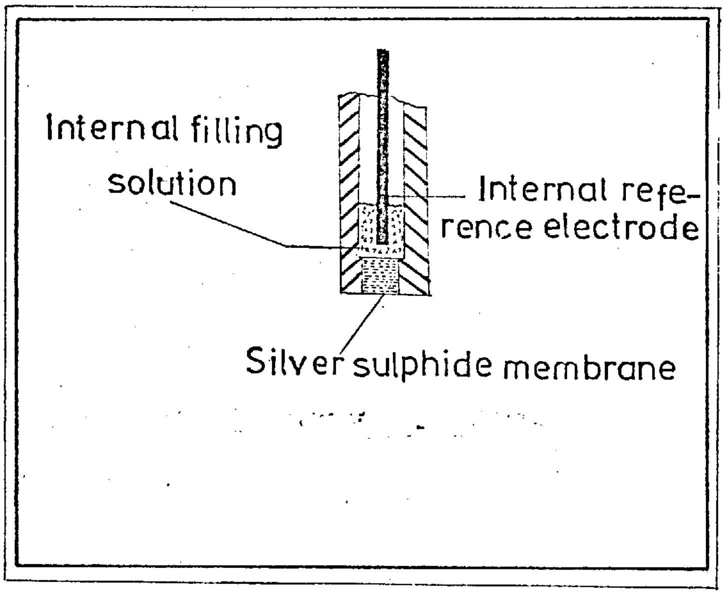

Fig. 3.9 Silver sulphide membrane electrode

$$E = K + 2.3 \times \frac{RT}{F} \times \log A_{Ag^+}$$

E is the measured potential of the system

K is the constant for the electrodes and solutions used

R is the universal gas constant

T is the absolute temperature

F is the Faraday constant

A_{Ag^+} is the activity of the silver ion in the sample

For samples which contain no silver ions, a very few are produced by very low solubility of the silver sulphide membrane (Hseu and Rechnitz, 1968). The silver ion activity depends on the sulphide ion activity in the sample solution and can be calculated from the solubility product (K_{SP}) of silver sulphide:

$$A_{Ag^+} = \sqrt{K_{SP}/A_{S^{2-}}}$$

(The solubility product of silver sulphide at 25°C is 1.48 ± 0.1 x 10^{-51} according to Hseu and Rechnitz, 1968.)

Nernst's equation above can be rewritten as:

$$E = \text{constant} - 2.3 \times \frac{RT}{F} \log A_{S^{2-}}$$

The constant is the same as in the previous Nernst equation except that it now contains an additional factor involving the solubility product of silver sulphide.

The electrode system measures the activity of sulphide ion. The concentration may be calculated if the ionic strength of the sample solution is known. The concentration is related to the activity by the following equation:

$$C_{S^{2-}} = (Y_{S^{2-}}) \times (A_{S^{2-}})$$

where $Y_{S^{2-}}$ is the sulphide ionic activity coefficient. As mentioned above the concentration of sulphide ion in any aqueous solution is related to the concentrations of hydrosulphide and hydrogen sulphide and is function of pH of the sample solution and is determined by the equilibrium constants of the reaction:

$$H_2S \rightleftharpoons H^+ + HS^-$$

$$HS^- \rightleftharpoons H^+ + S^{2-}$$

$$\frac{C^2_{H^+} \times C_{S^{2-}}}{C_{H_2S}} = K_{H_2S}$$

If the pH of a solution is known and the concentration of S^{2-} is determined, then the concentration of hydrogen sulphide may be calculated as below:

$$\log C_{H_2S} = \log C_{S^{2-}} - \log K_{H_2S} - 2pH$$

A reference electrode, with or without a saltbridge, is used together with the indicator electrode and the potential developed is measured. In Fig. 3.10 a typical sulphide titration curve is given.

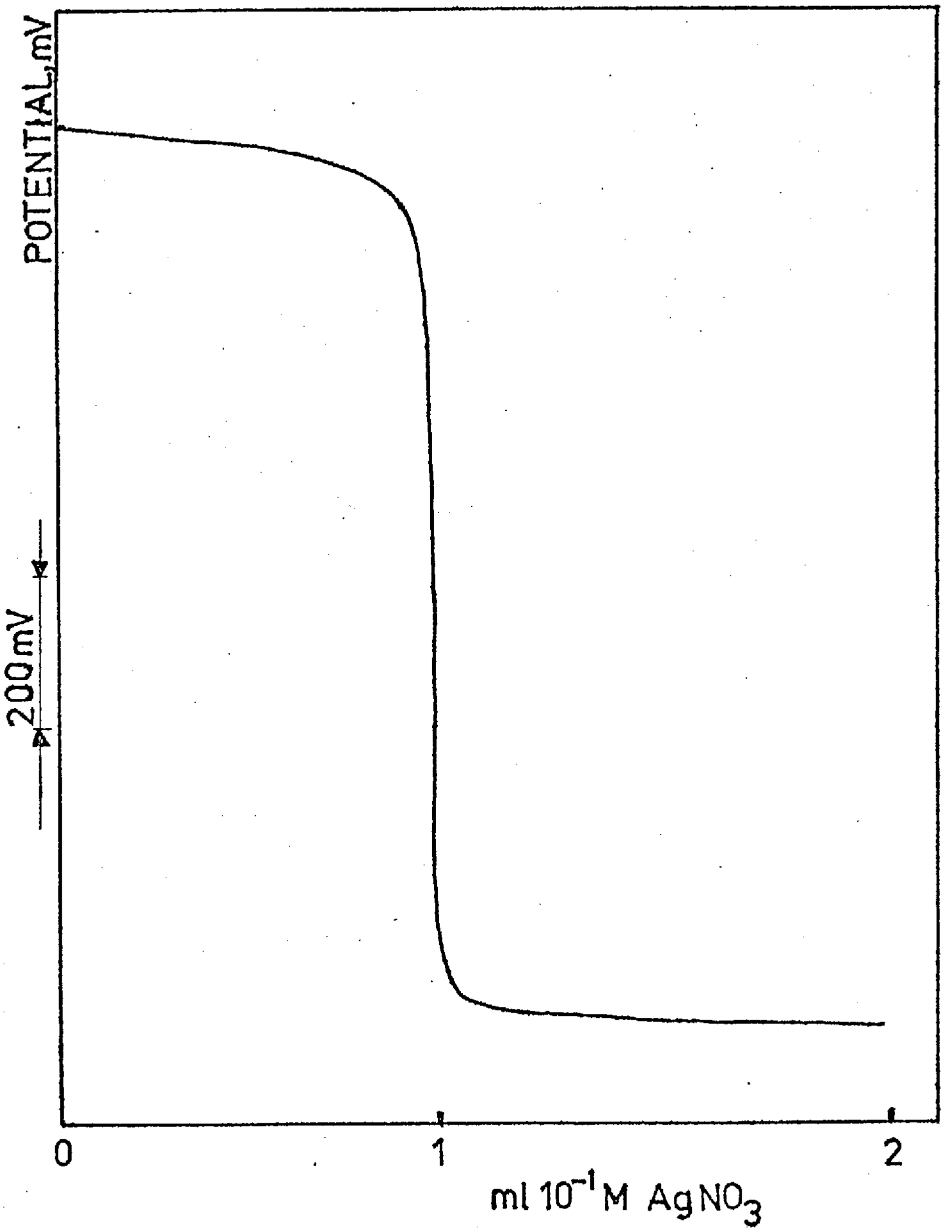

Fig. 3.10 Sulphide titration curve (after Pungor et al, 1968)

Allam et al (1972) used a sulphide-ion selective electrode determining hydrogen sulphide concentrations in submerged soils. They found hydrogen sulphide concentrations in the range 0.05 - 641.28 ppb and that the two main factors controlling hydrogen sulphide concentration in soil were soil pH and oxidizable carbon. Morie (1971) employed a specific sulphide-ion electrode in the determination of hydrogen sulphide in cigarette smoke. Other workers such as Bock and Puff (1968) report successful results using the sulphide-ion selective electrode in sulphide determinations as well.

Table 3.2 shows important characteristics of the sulphide-ion selective electrode.

Table 3.2 Characteristics of the silver-sulphide membrane electrode (Allam et al, 1972)

Concentration range	10^{-0}-10^{-7} total silver or sulphide 10^{-0}-10^{-25} free silver or sulphide
Temperature range	0 - 100°C
pH range	0 - 14
Slope at 25°C	29.6 mV/sulphide/decade 59.2 mV/silver/decade
Transient response time	5m sec - 2 min
Interferences	sulphide ion: none silver ion: Hg^+
Temperature coefficient	+ 0.05 mV/°C in 0.1M Na_2S or in 1.0M NaS - 0.40 mV/°C in 0.1M $AgNO_3$
Resistance	0.5 - 1 megohm

CHAPTER 4

ANALYTICAL RESEARCH AND DEVELOPMENT

4.1 Introduction

Analytical work has been carried out, testing and modifying the sensitive wet-chemical colorimetric methods for sulphur dioxide and hydrogen sulphide described in Chapter 3. The methods were modified in attempts to improve the sensitivity for use in ambient air and soil atmosphere measurements and to simplify the procedures for application in the field. The determination of sulphur gases in the lower ppb concentration range is not simple from an analytical point of view and progress was necessarily slow. Erratic and spurious results may be caused by factors such as photodecomposition, oxidation and adsorption in the sampling system. Efforts to eliminate or to reduce the effects of these parameters were made.

4.2 Experimental Work

4.2.1 Sampling apparatus and procedure

Air was drawn into a sampling system with the aid of a Capex Mark 2 reciprocating 12 volt suction pump, powered by a car battery. The air-stream was drawn through polyvinyl chloride (PVC) and glass tubes into the bubblers, containing potassium tetrachloromercurate absorbing solution for sulphur dioxide and cadmium hydroxide absorbing solution for hydrogen sulphide. The flow-rate was controlled by an adjustable airmeter, connected to the sampling system outlet, thus avoiding contact between adsorptive surfaces and the air-stream. The sampling system is illustrated in Fig. 4.1.

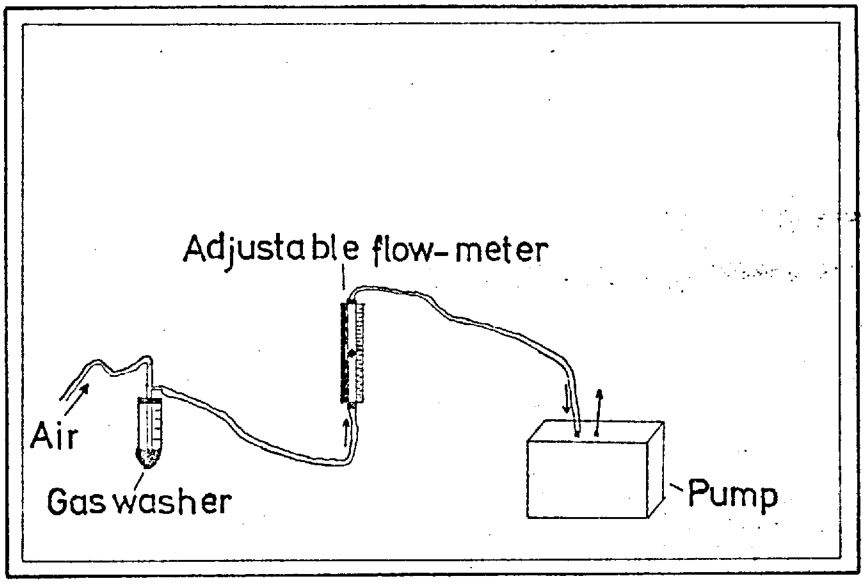

Fig. 4.1 Sampling apparatus for atmospheric gases.

Three different types of bubblers were used. In all of them, air was drawn through a tube immersed in the absorbing solution. Sulphur dioxide and hydrogen sulphide in the air-stream were subsequently trapped in the tetrachloromercurate and cadmium hydroxide absorbing solutions. For greatest efficiency in absorption, capillary tubing producing small bubbles was used in all types of gas washers. The volume of the final solutions were reduced to 5 ml, which will be described below, and graduated 5 ml V-shaped centrifuge tubes were used as scrubbers. When larger volumes of final solutions were occasionally used, a Gelman test tube or a midget bubbler was employed.

4.2.2 Analysis of sulphur dioxide

4.2.2.1 Introduction

As previously stated, because of its high sensitivity, simplicity and presumed applicability to mineral exploration vapour geochemistry, the West-Gaeke colorimetric method was selected.

The original method was modified in an attempt to increase the sensitivity and to simplify the working procedure, making the method applicable to field operations. All reagent concentrations have been standardized to allow an addition of 1 ml. The principle procedure of the modified method follows the routine as for the original.

4.2.2.2 Procedure and tests carried out with the West-Gaeke method

A total volume of 5 ml was used instead of 25 ml as prescribed in the original method to improve sensitivity.

An air-stream was drawn into the sampling system with the aid of a suction pump at a rate of 0.5 l/min and bubbled through 2 ml of a 0.04M potassium tetrachloromercurate solution (TCM), contained in a 5 ml graduated, V-shaped centrifuge tube. After sampling, 1 ml of 0.12% sulphamic acid was added and mixed. Thereafter, the solution was allowed to stand for 10 minutes to ensure complete destruction of interfering nitrites. Thereafter, 1 ml of 0.016% hydrochloric-bleached pararosaniline hydrochloride (PRA) was added, followed by the addition of 1 ml 0.08% formaldehyde solution. About 30 minutes were allowed for reaching an optimal colour development. The absorbance of the pararosaniline methyl sulphamic acid complex was finally measured spectrophotometrically at 5480 Å. Scaringelli et al (1967) recommended this wavelength instead of the one suggested by West and Gaeke (1956) for solutions containing pararosaniline hydrochloride.

Initially an SP 600 Spectrophotometer was used, but was later replaced by the more rapid Gilford Spectrophotometer. The former instrument was, however, always used in the measurements of the soil-air samples collected in the fieldwork, because of its portability in a field laboratory.

The pararosaniline dye was recrystallized from aqueous methanol prior to use to remove impurities in the base as reported by other researchers. The cleaning procedure is described below.

> Pararosaniline hydrochloride was dissolved in 250 ml of 2.5N hydrochloric acid for the removal of impurities. After about 2 hours the bleached solution was filtered. Weakly, yellow-coloured and shiny plates precipitated. A slight excess of 2.5N sodium hydroxide solution to the filtrate resulted in a removal of the yellow colour. The base was then carefully rinsed with deionized water and finally recrystallized in 70 ml of boiling methanol to which 300 ml of deionized water was added at 80°C. The solution was cooled at room temperature.

Standard sulphite solutions for calibration were prepared daily owing to the rapid decomposition of the sulphite with time. The procedure has been described by Scaringelli et al (1967). 0.400g of sodium sulphite was dissolved in 250 ml of freshly boiled and cooled deionized water. The concentration of the sulphite solution was determined iodometrically and back-titrated with 0.1N sodium thiosulphate which had been standardized against a potassium iodate solution of known concentration.

The sulphite solution was stabilized by dilution with tetrachloromercurate (TCM) directly after the analysis, following the procedure below.

2 ml of the standard solution were diluted to 100 ml with TCM. Aliquots of 0, 1, 2, 3, 4 and 5 ml were transferred to 25 volumetric flasks, followed by the addition of 5 ml 0.12% sulphamic acid. After 10 minutes, 5 ml each of 0.08% formaldehyde solution and 0.016% pararosaniline were added. After the addition of TCM to the 25 ml mark, 30 minutes were allowed for maximum colour development. The intensity of the colour was measured spectrophotometrically at 5480 Å. A typical standard curve is illustrated in Fig. 4.2, showing absorbances versus concentration.

The same batch of the purified dye was used in all calibrations and tests. Owing to the instability of the sulphite- and formaldehyde solutions, new calibration curves had to be prepared daily. All the other reagents have been claimed to be stable for months. Analytical grade chemicals were always used.

In order to investigate the efficasy and reproducibility of the TCM absorbing solution and the method respective-

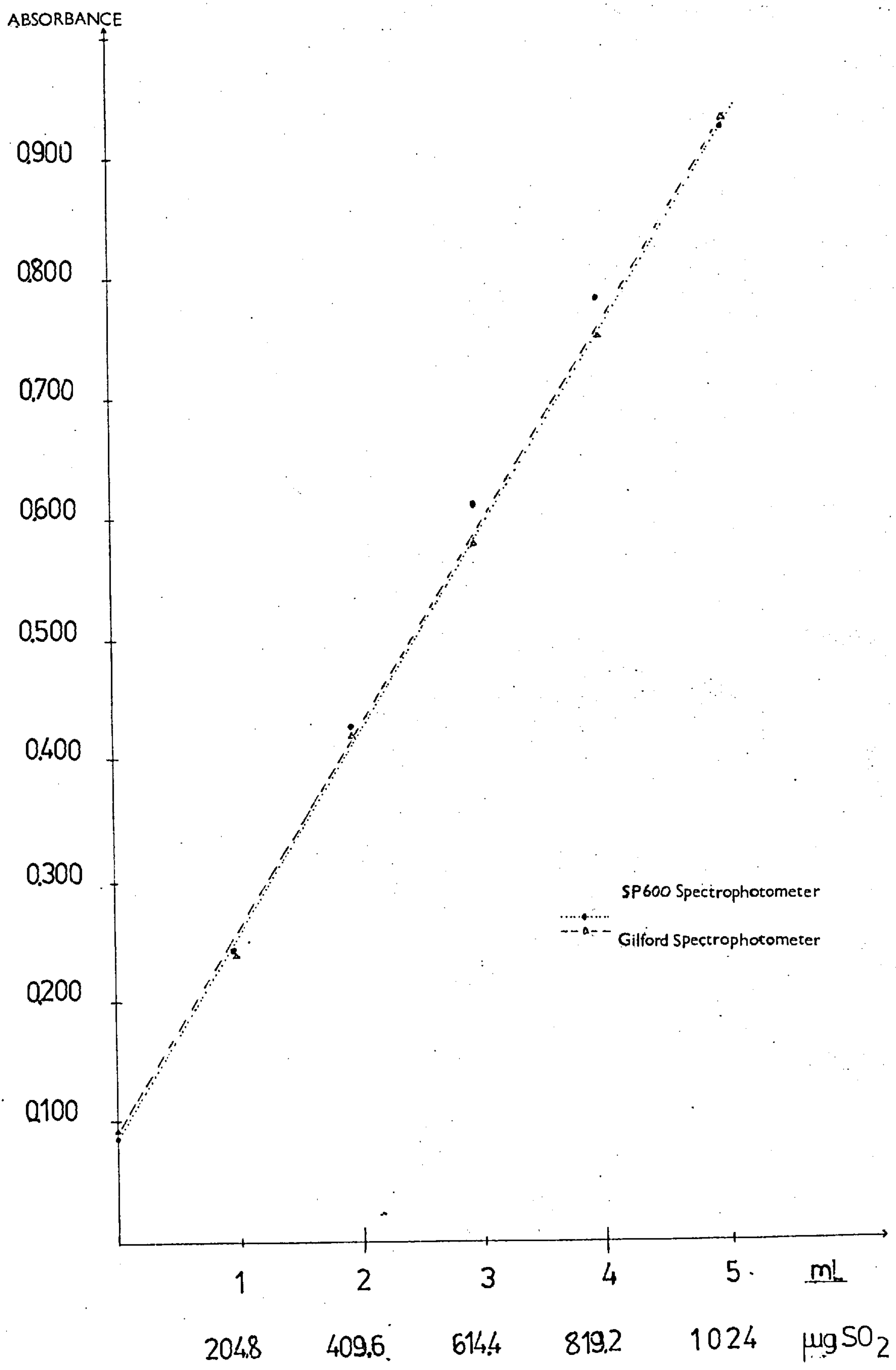

Fig. 4.2 Calibration curve for SO_2

ly permeation tubes containing liquid sulphur dioxide were prepared. A fluorinated ethylene (*PTFE Teflon) tube of about 10mm length with an inner diameter of 1.5mm was sealed at one end with two glass beads. The tube was filled with sulphur dioxide, obtained from a 250 ml cylinder and cooled to liquidity at -10°C with solid carbon dioxide. After filling, the sulphur dioxide was enclosed in the tube by sealing the remaining open end with two glass balls. After sealing, diffusion takes place through the permeable walls. The diffusion rate is constant as long as liquid and gas are in equilibrium. The concentration evolved may be varied by changing the length or wall thickness of the tube and temperature or the flow of the sweeping carrier gas. Diffusion or permeation rates were found to change from tube to tube. In general, the life-length of a tube was one or two days when stored at room temperature. The life was prolonged, if the tubes were kept in a refrigerator. In the tests, sulphur dioxide free-air was used as a carrier gas.

The figures below illustrate the sampling apparatus in use as well as a permeation tube (Figs. 4.3 - 4.4).

Air was drawn into the sampling system with the aid of a small suction pump. Sulphur dioxide, present in the atmosphere, was trapped immediately in a solution of TCM, contained in a conical flask. The clean air-stream was swept through a vessel containing the sulphur dioxide permeation tube. The evolved sulphur dioxide was subsequently absorbed in a 5 ml v-shaped scrubber containing TCM. The inlet flow-rate was controlled by an adjustable flow-meter as well as the

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*PTFE = polytetrafluor ethylene

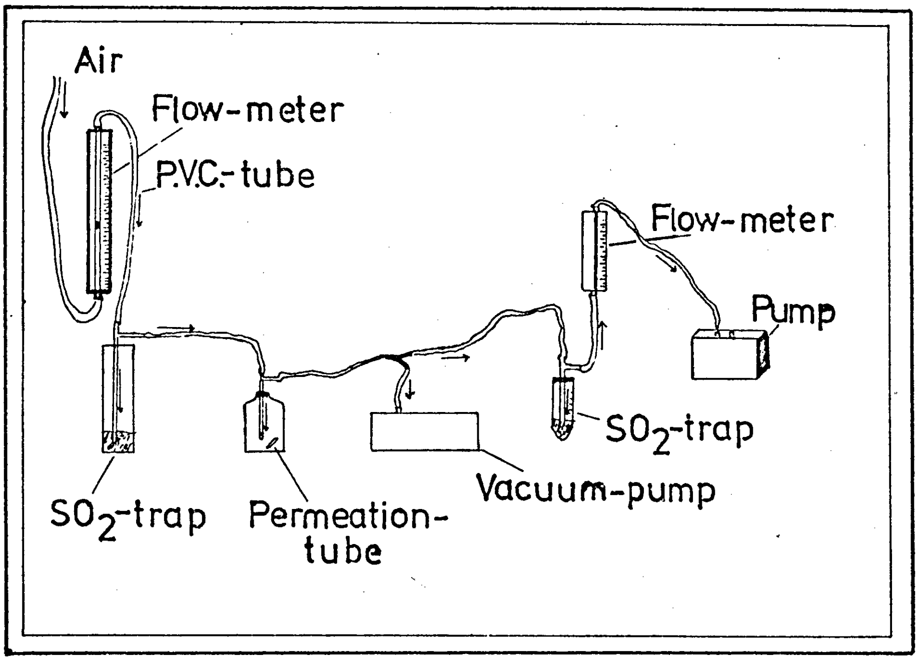

Fig. 4.3 Sampling device for SO_2

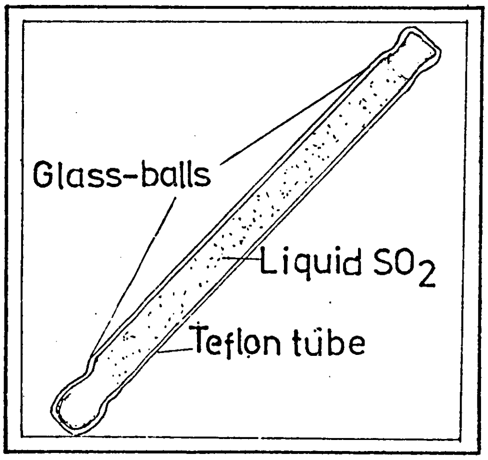

Fig. 4.4 SO_2 permeation tube

outlet flow-rate. A vacuum pump was used for dilution purposes. A constant flow-rate through the bubbler was maintained, while the sampled volume varied. Numerous permeation tubes were consumed in the investigation. Spurious results of sulphur dioxide concentrations were received for one and the same permeation tube, probably owing to an irregular emission of the volatile compound and also by adsorption of the gas on the PVC tube. The variance of the concentrations recovered is shown in Table 4.1.

In calculating the concentration, the following formula was applied from Scaringelli et al (1967):

$$\mu g\ SO_2/ml = 0.88 \times (\text{Sample absorbance-Blank absorbance}) = a$$

$$\mu g\ SO_2 \text{ in } 5\ ml = 5 \times a$$

$$ppb = \frac{5 \times a \times 0.382 \times 1000}{\text{volume of sampled gas (in } \ell)}$$

0.88 is the calibration factor (reciprocal of the slope of the calibration curve). This value may be used in calculations provided there are no changes in pH and temperature.

0.382 is the volume ($\mu\ell$) of 1 μg sulphur dioxide at 25^oC, 760mm Hg.

In the following tests, all permeation tubes were weighed on a Stanton Microbalance B.A.5 before and after sampling. Flow-rates presented with tables are the flow-rates of the air-stream through the gas washer.

The theoretical sulphur dioxide concentration in the gas stream may be calculated according to the formula below.

The following equation permits calculating ppm permeand as a function of air flow-rate over the tube.

$$C(\text{ppm}) = \frac{R}{F} \times \frac{22.4}{M} \times \frac{T}{273} \times \frac{760}{P}$$

C = ppm (v/v) of permeand transferred to a carrier gas flowing over the tube

R = permeation rate

F = Gas flow-rate

22.4 = Molar gas volume at S.T.P.

M = Molecular weight of gas compound in tube

T = Temperature at which F is measured

P = Pressure at which F is measured

At 25^{o}C and 760mm Hg, the equation may be simplified to the following:

$$C(\text{ppm}) = \frac{R}{F} \times K$$

K = a constant that amounts to a value of 0.382 for sulphur dioxide. 0.382 is the volume (μℓ) of 1 μg sulphur dioxide at 25^{o}C, 760mm Hg.

$$C(\text{ppb}) = \frac{R}{F} \times K \times 1000$$

An inlet flow-rate of 5.0 ℓ/min was maintained, giving a dilution of 1:10 of the air-stream passing through the bubbler,

Table 4.1 Measurements of SO_2 concentrations emitted from a permeation tube using a constant flow-rate (0.5 ℓ/min) and different volumes

Number	Time (min)	Volume (ℓ)	Concentration (ppb)	% Recovered
Deionized water			0	
1	30	15	141.2	90.1
2	10	5	228.6	100.0
3	20	10	181.2	100.0
4	10	5	144.6	92.2
5	30	15	91.3	58.2
6	20	10	25.9	16.5
7	10	5	82.0	52.3
8	10	5	67.9	43.3
9	20	10	74.8	47.7
10	30	15	76.6	48.9

since the flow-rate through the bubbler was 0.5 ℓ/min. The air-stream was found to contain 1568 ppb sulphur dioxide, of which one tenth was supposed to enter the gas washer (the loss of sulphur dioxide was estimated by direct weighing to 390 μg during the total time of sampling).

When a constant flow-rate as well as a constant volume were used, the concentrations of sulphur dioxide were found to be more homogeneous. A difference of about 40% was observed between the highest and the lowest concentration recovered (Table 4.3).

Further tests were carried out weighing the permeation tubes on a LM-500 Micro Balance instead of the Stanton instrument. The latter had been shown to give unrepeatable values when weighing a 1g weight several times. A maximal difference of 260 µg was observed, making the instrument less than suitable for regular weighings to determine the loss of sulphur dioxide per minute.

Successive weighings of a 0.500g steel plate, using the LM-500 balance, gave the same results each time. The graph below (Fig. 4.5) illustrates the loss of sulphur dioxide versus the time of a typical permeation tube containing liquid sulphur dioxide.

Table 4.2 Sulphur dioxide permeation rate from a fluorinated ethylene (PTFE Teflon) permeation tube

Time (min)	Weight (g)	Loss (µg)	Loss/Time-unit (µg/min)	Incremental loss (µg/min)
0	0.938920	0	0	0
55	0.938570	350	6.36	6.36
80	0.938400	520	6.41	6.80
100	0.938280	640	6.40	6.00

The final permeation tube investigations were made under more controlled conditions as compared with the initial tests. Before discussing the results of this work, a short presentation is given describing the different steps taken. Calculations used, when estimating the concentration of sulphur dioxide evolving from a permeation tube has been described on

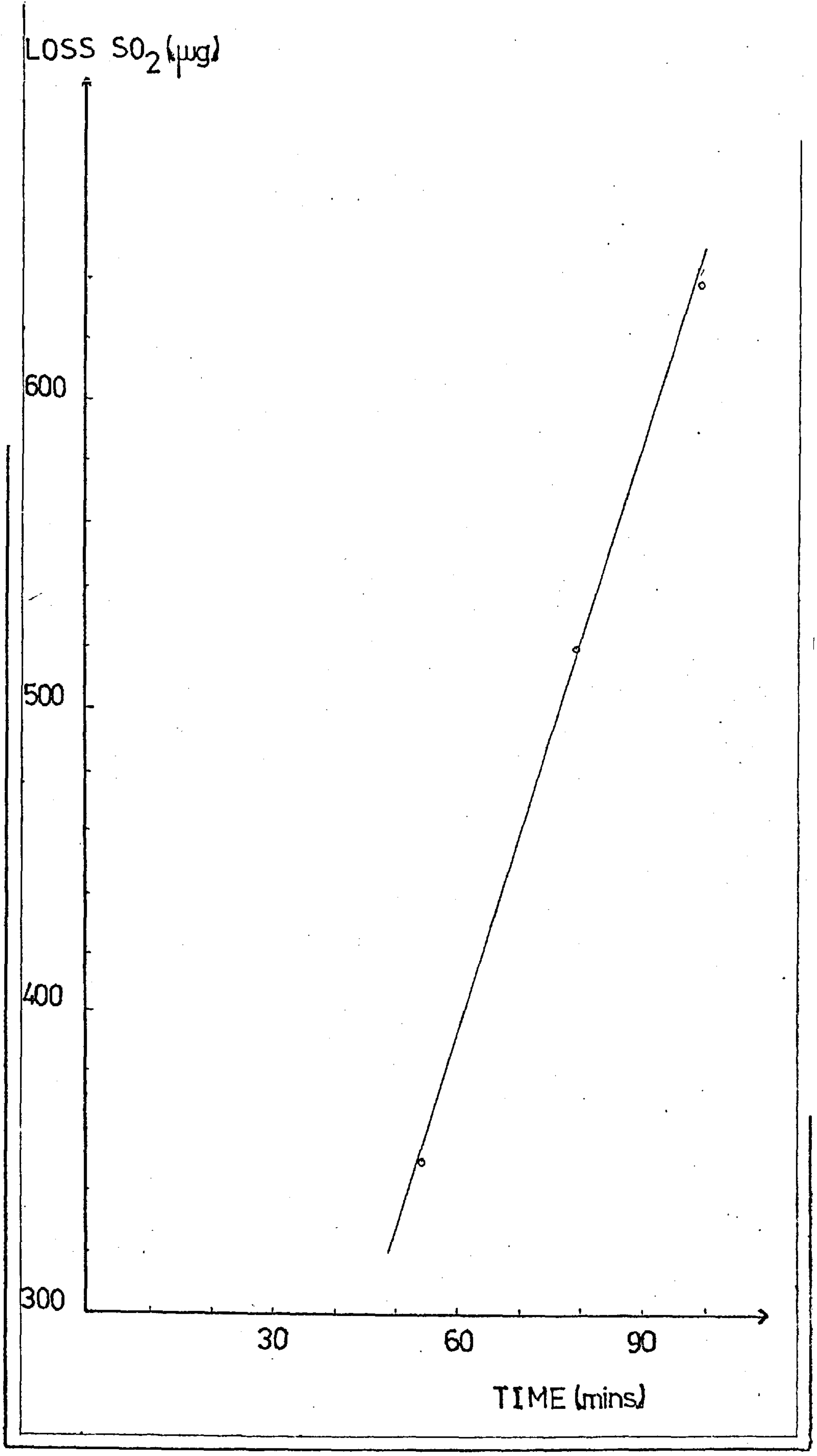

Fig. 4,5 Loss of sulphur dioxide versus time (Measurements carried out on a LM-500 Micro Balance) p.73. Initially a calibration curve was prepared in the usual manner. A permeation tube was thereafter weighed and the loss per time-unit calculated. In the following tests, the trap for the atmospheric sulphur dioxide was replaced with a graduated, 5 ml V-shaped centrifuge tube. The permeation-tube container was immersed in a cold-water bath. The permeation-rate of the tube was calculated to 2.9 µg/min and the flow-rate sweeping the sulphur dioxide was 5 ℓ/min. Sampling was 0.5 ℓ/min. The equation below gives the concentration evolved in ppm:

$$C = \frac{2.9}{0.5} \times 0.382 = 2.22$$

Table 4.3 shows the sulphur dioxide recovered in the TCM absorbing solution. A volume of 5 ℓ was maintained for all samples.

Table 4.3 Percent SO_2 recovered of a known emission from a permeation tube using a constant flow-rate (0.5 ℓ/min) and sample volume (5 ℓ)

Number	Concentration (ppb)	% Recovered
1	123.4	55.5
2	130.8	58.9
3	119.7	53.9
4	126.7	57.1
5	99.8	45.0
6	150.3	67.7
7	187.5	84.5
8	136.5	61.5
9	105.2	47.4
10	142.2	64.1
Air	7.5	

The concentration of sulphur dioxide in air is calculated on basis of a volume of 50 litres, sampled at a rate of 0.5 ℓ/min. Fig. 4.6 illustrates the dispersion of sulphur dioxide using a constant flow-rate and sample volume.

The same permeation tube was weighed after 18 hours and after another 8 hours. The permeation-rate was found to be constant. In the following test, a flow-rate of 0.5 ℓ/min was maintained, while the sample volume varied from 2.5 litres to 20 litres. The inlet flow-rate was 5 ℓ/min giving a dilution of 1:10 of the sulphur dioxide passing on to the TCM absorbing solution. Fig. 4.7A illustrates the sulphur dioxide concentrations recovered versus sample volume.

The recovery of sulphur dioxide in the TCM absorbing solution of a known amount of gas evolved from a cooled permeation tube was observed to be in the range 38 - 39 percent. Low sampling volumes gave the highest recovery (Fig. 4.7B). Some part of the loss is probably due to photodecomposition and adsorption in the sampling system. Other reasons may be errors in the weighings of the permeation tubes, poor mixing of the gases (sulphur dioxide and air-stream), oxidation may play a part and therefore it is not necessary that large volumes give lower detection limits. Nevertheless, the method would find an application in the detection of sulphur dioxide in the soil atmosphere and in pollution control.

All work using permeation tubes has taken place after all fieldwork.

One parameter for defining performance is the limit of detection. Thompson and Howarth (1976) define the detection

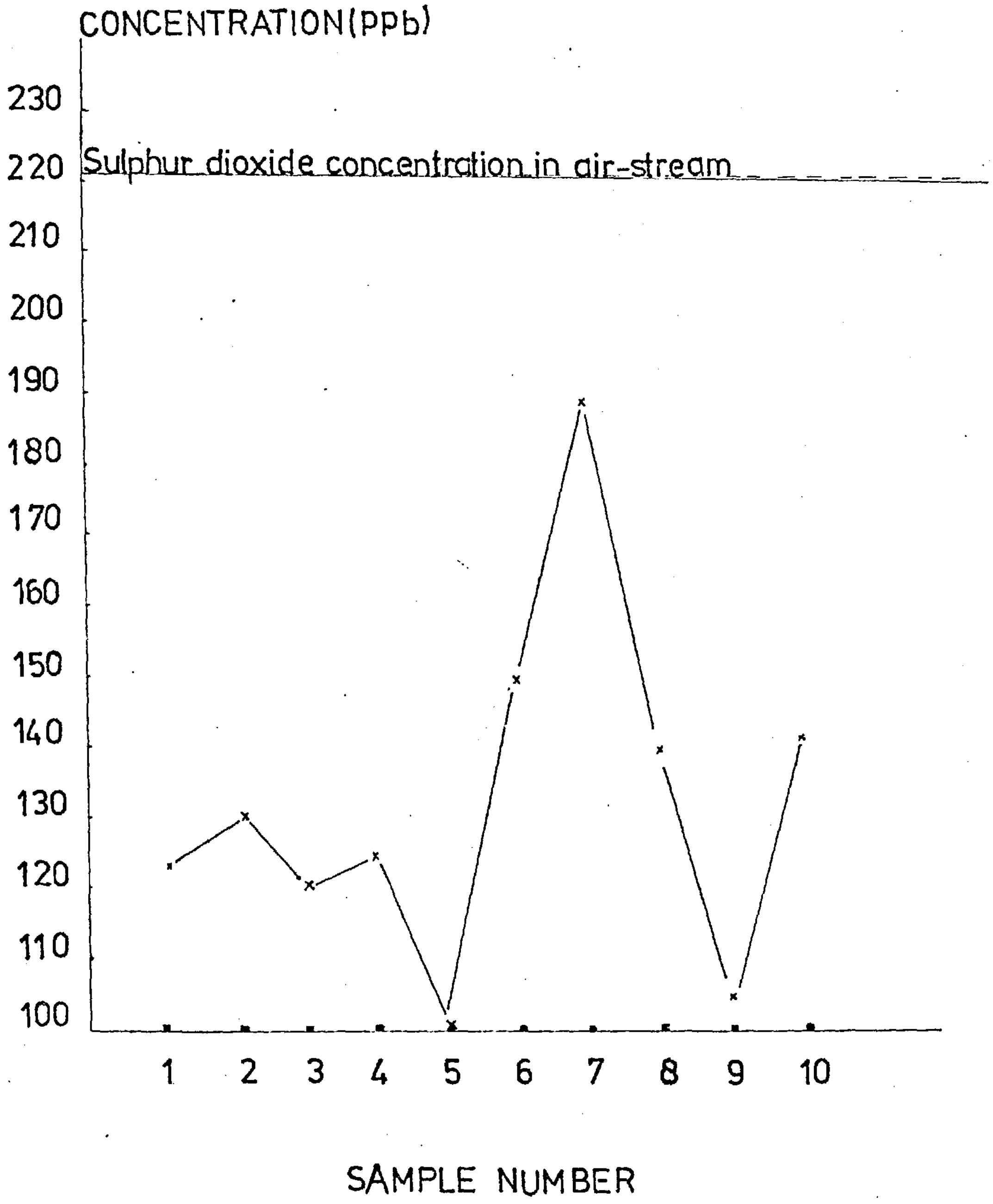

Fig. 4.6 Sulphur dioxide concentrations recovered from a known amount evolved from a permeation tube when using a constant flow-rate and sample volume.

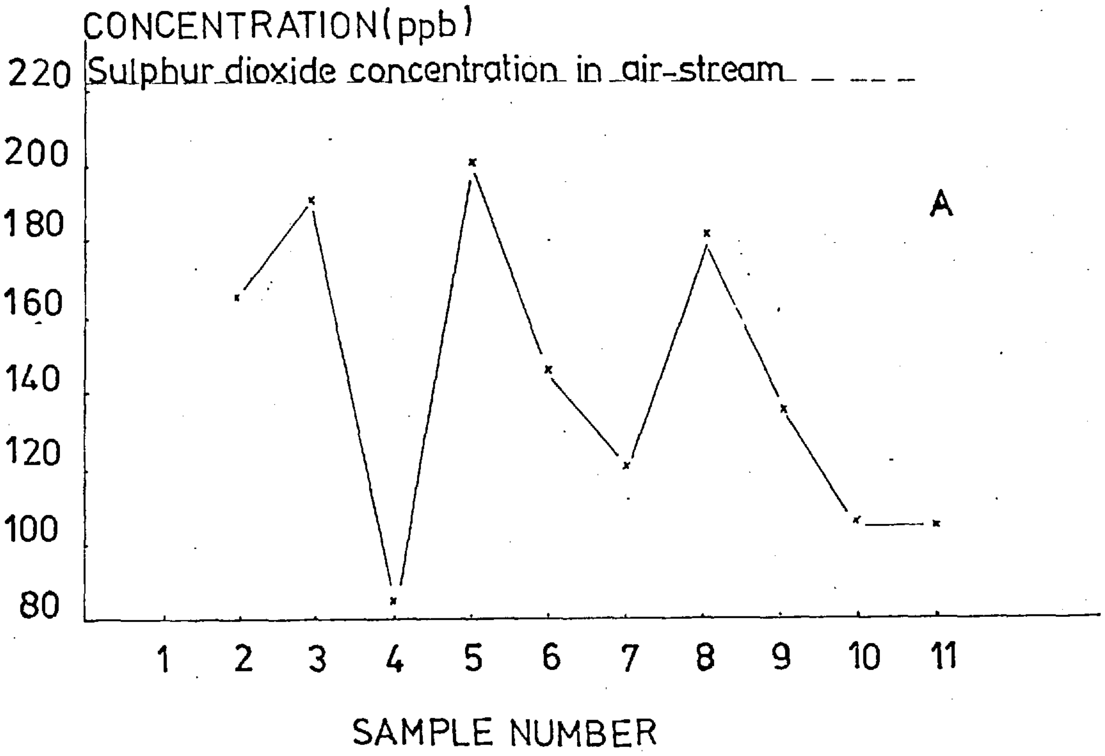

Fig. 4.7A SO_2 concentrations recovered from a known amount using a constant flow-rate but different sample volumes

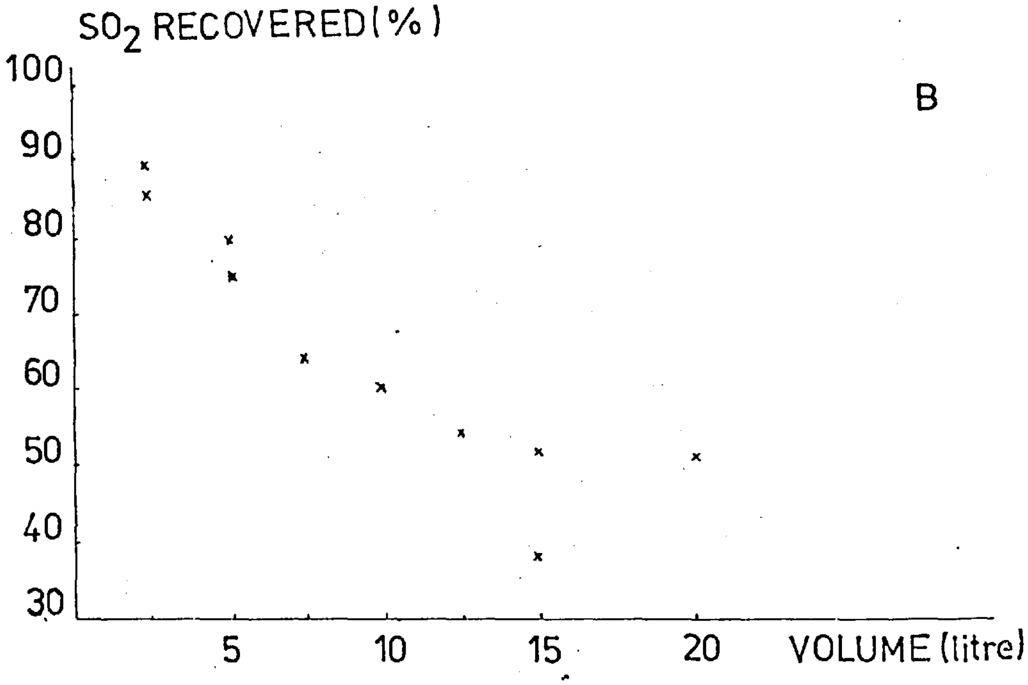

Fig. 4.7B Percentage SO_2 recovered versus sample volume.

limit as 2 x the standard deviation near zero concentration. In order to determine this value, a series of tests was carried out measuring low sulphur dioxide concentrations using a permeation tube immersed in a cool bath. The measured concentrations that have been used in the calculations are presented in Table 4.4. A flow-rate of 0.5 ℓ/min with a volume of 5 ℓ was used.

Table 4.4 Low SO_2 concentrations measured in a gas stream sweeping over a permeation tube.

Number	Concentration (ppb)
1	3.03
2	1.01
3	1.01
4	2.02
5	4.71
6	4.37
7	1.01
8	3.70
9	2.02

The standard deviation, calculated on basis of the concentration values in Table 4.4, is 1.48 giving the limit of detection to 3 ppb for a 5 ℓ sample following the definition by Thompson and Howarth (1976).

4.2.3 Analysis of hydrogen sulphide

4.2.3.1 Introduction

In the analysis of hydrogen sulphide, two methods have been tested. A detailed description of the laboratory work carried out using the methylene blue colorimetric method and the sulphide-ion selective electrode is presented below. The former was found to have applicability in the field operations owing to its simplicity and low cost.

4.2.3.2 Procedure and tests carried out with the methylene-blue colorimetric method

In order to simplify the method for application in the field and to improve sensitivity, it was found convenient to reduce the final solution to 5 ml from 25 ml as suggested in the original procedure. All chemicals, except ferric chloride, were standardized to 1 ml aliquots. Initially, one drop of ferric chloride was used, but was later replaced with a precise amount of 30 µl, added with the aid of an Eppendorf micropipett to improve reproducibility.

Analytical grade chemicals were used and diluted in freshly boiled nitrite-free deionized water. All solutions were stored in a refrigerator when not in use. The deionized water was made nitrite-free by adding sulphamic acid (50 mg/ℓ). This solution as well as the unstable sulphide solution for calibration purposes were prepared daily.

In the separation of hydrogen sulphide from air, the following procedure was applied. One ml each of sodium hydroxide (0.6 g/ℓ) and cadmium sulphate (8.6 g/ℓ) were added to a graduated, 5 ml V-shaped centrifuge tube. Thereafter, the air-stream to be sampled was bubbled through the absorbing solution of cadmium hydroxide. Hydrogen sulphide, if present in the air, was subsequently trapped and a precipitate of cadmium sulphide was formed. When 1 ml amintest solution (3.45g p-aminodimethylaniline in 1 ℓ of 1:1 sulphuric acid) was added, hydrogen sulphide was released. 30 μl ferric chloride (1g/ml) were then added and methylene blue was formed. The volume was made up to 5 ml with nitrite-free deionized water. About 30 minutes were allowed for colour development, after which the optical density was measured at 6700 Å on a spectrophotometer.

In the preparation of standard curves, a three-step procedure was applied as follows below. A sodium sulphide solution containing about 1 μg sulphide per ml was prepared, followed by the addition of aliquots of 0, 1, 2, 3, 4 and 5 ml of the sulphide solution to the absorbent. Thereafter, the amintest solution, ferric chloride and deionized water were added.

The sodium sulphide solution was prepared by diluting a solution containing about 0.1 mg hydrogen sulphide equivalent per ml, which in turn had been prepared by dissolving 0.353 g sodium sulphide in 500 ml nitrite-free deionized water. The strength of the sodium sulphide solution was determined by titration of a 25 ml sodium sulphide solution, to which had been added 50 ml 0.01N iodine and 10 ml 0.5M hydrochloric acid, with 0.01N sodium thiosulphate. After calculating the concentration of the sulphide solution, the calibration curves were prepared as follows:

The reagents were added with either a 1 ml pipette or with a 250 ml Oxford laboratories dispensor. The latter was, however, observed to give varying amounts of solution resulting in a wide absorbance variation and therefore was subsequently replaced entirely by the pipette. The absorbance was measured spectrophotometrically on an SP600 spectrophotometer and a Gilford microsampling spectrophotometer. As the latter instrument is more rapid, it was used in most experiments. The former instrument was, however, used in all determinations of samples collected in the field. The variation of the performance on the two instruments is shown in Fig. 4.8.

It was found that sulphide was rapidly oxidized in the alkaline absorbent of cadmium hydroxide during sampling. After passing air at a rate of 1 ℓ/min for 30 minutes only about 38% of a known concentration of sulphide remained (curve 1 on Figs. 4.9 - 4.10). The oxidation of the sulphide was reduced, but not eliminated, by the addition of 1% of the antioxidant arabino-galactan. Curve 2 on Figs. 4.9 - 4.10 illustrates this improvement. Further modifications included the bubbler being kept in darkness, giving a recovery of 52% after 30 minutes bubbling at a rate of 1 ℓ/min (curve 4 on Figs. 4.9 - 4.10). The oxidation was further reduced by using an absorbing solution to which 2% arabino-galactan had been added and the bubbler was kept in an ice-bath (curve 5 on Figs. 4.9 - 4.10). After 30 minutes bubbling at a rate of 1 ℓ/min about 69% of the sulphide remained. In the

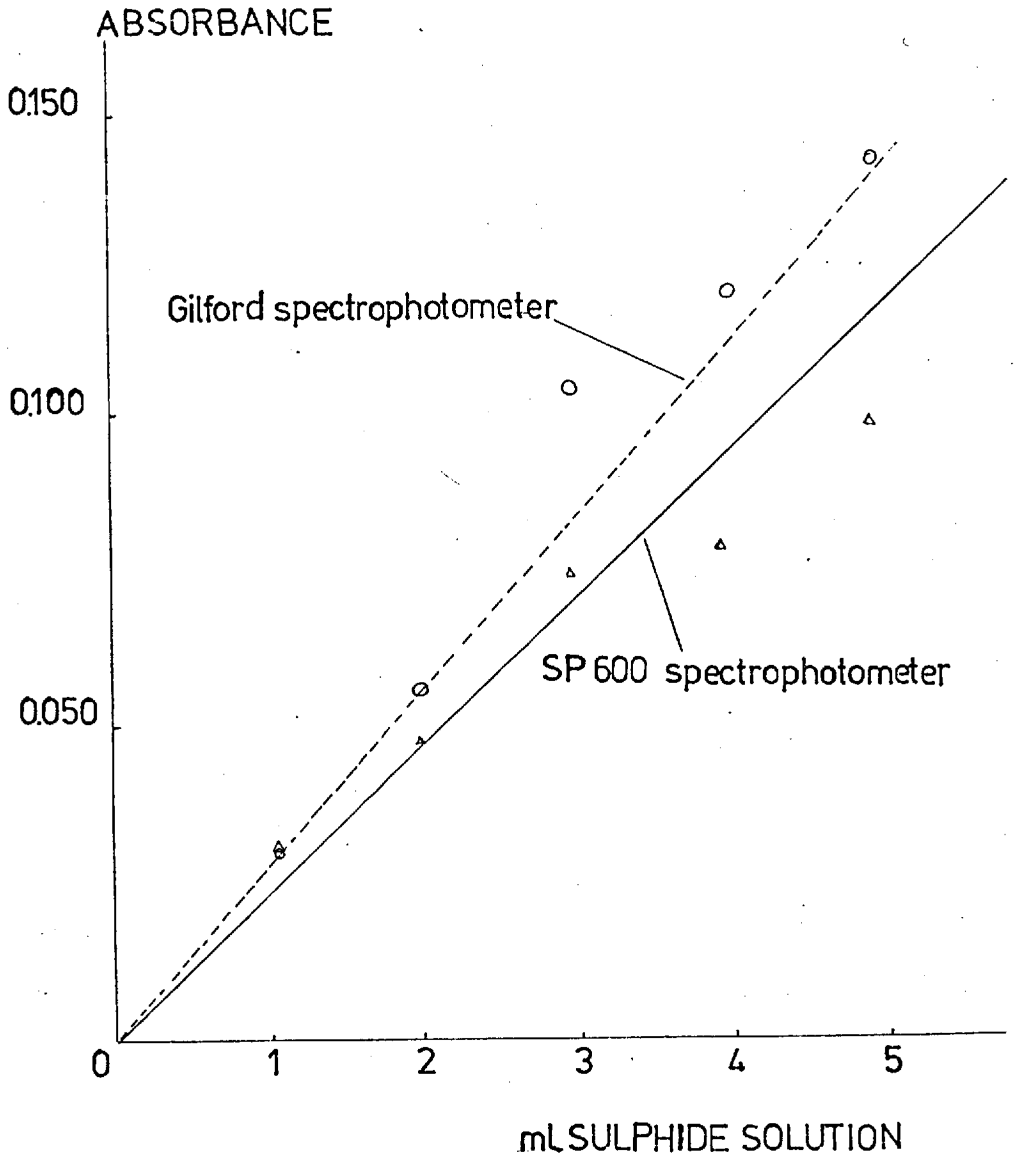

Fig. 4.8 Calibration curve for H_2S

following tests, the washers were stored in darkness and immersed in an ice-bath. Antioxidants such as 2% glucodine and 0.2M ascorbic acid were tested, but were found to be useless or to interfere with the methylene blue formation.

The increase in sulphide concentration after 30 minutes bubbling as illustrated by the curves on Figs. 4.9 - 4.10 might be explained as below.

In the tests, bubbling times of 5 - 30 minutes were used, beginning with the lowest. After bubbling, the samples were stored at room temperature until analysis with the result that the first sample stood for about 100 minutes before analysis. The last sample stood only a few minutes. It is possible that a further decomposition, although slow, takes place in the samples after bubbling and that the brief time before the analysis of the last sample does not allow this decomposition to take place.

A description is presented below of calculations used in estimating the atmospheric sulphide concentration.

The concentration of hydrogen sulphide in the laboratory air was estimated in a volume of 45 litres, sampled at a rate of 0.5 ℓ/min. A 2 ml cadmium hydroxide absorbing solution was used to which 2% arabino-galactan had been added. The gas washer was kept in darkness and immersed in an ice-bath when sampling took place. The optical density was measured 30 minutes after addition of the reagents. An absorbance of 0.025 was measured giving a concentration of about 0.2 μg hydrogen sulphide (Fig. 4.11). The following calculations were used:

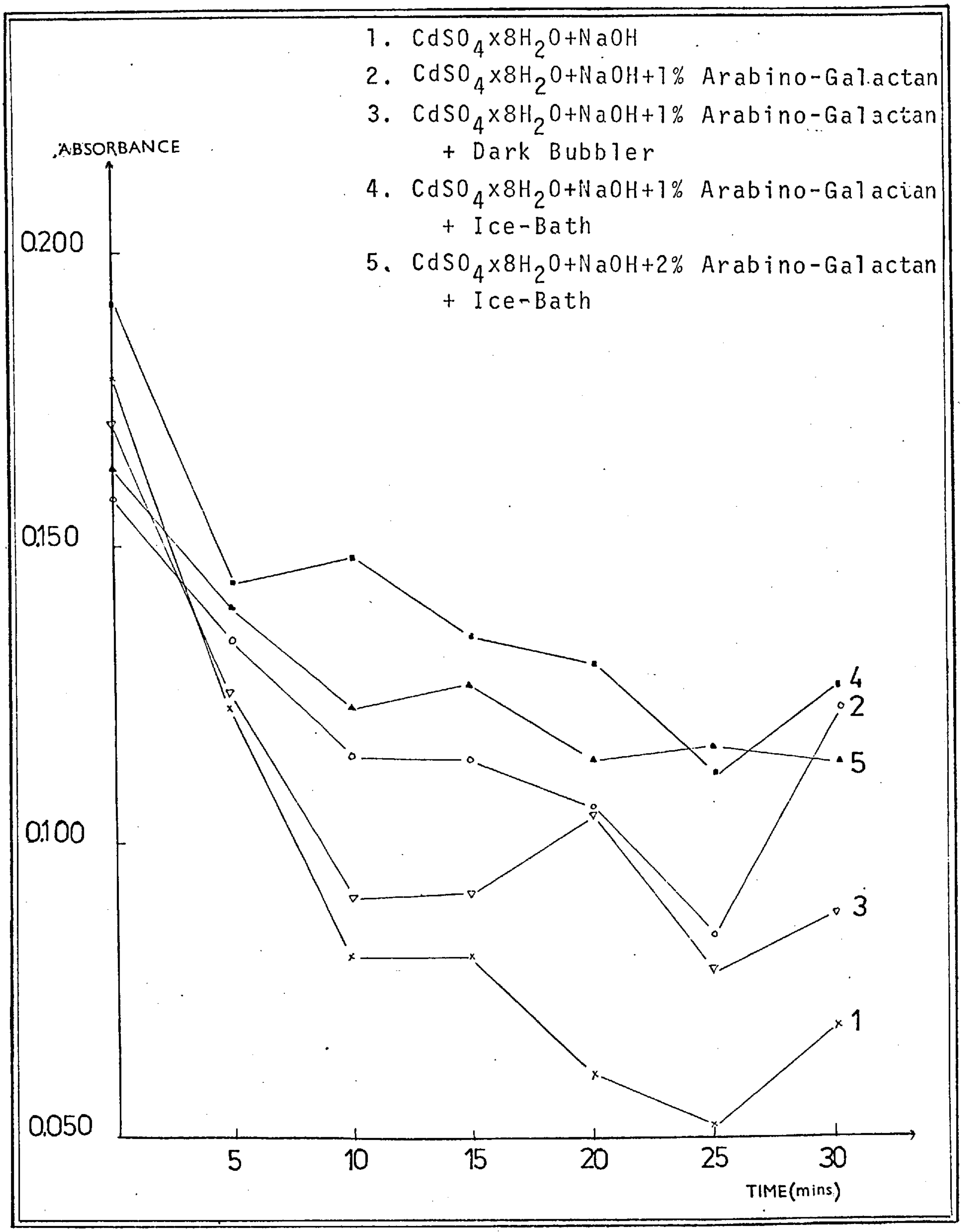

Fig. 4.9 Determination of the oxidation-rate in samples (5 ml) containing 0.2 µg/ml of H_2S

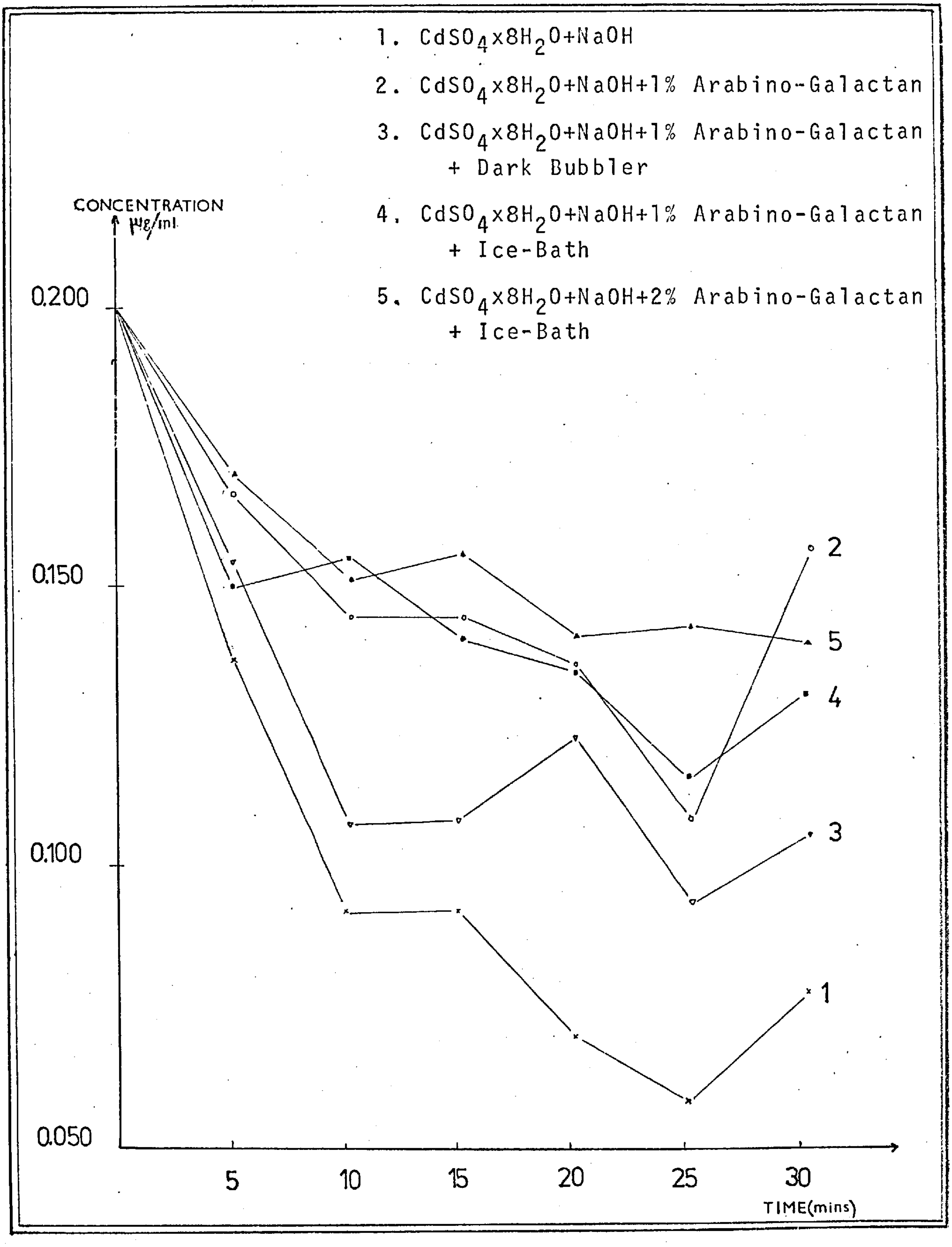

Fig. 4.10 Determination of the concentration-rate in samples (5 ml) containing 0.2 µg/ml of H_2S

At 25°C and 760mm Hg, there is

$$\frac{22.4}{34} \times 1000 \times 0.2 \times 10^{-6} \text{ ml } H_2S$$

$$= 13 \times 10^{-5} \text{ ml } H_2S$$

The concentration of hydrogen sulphide in 45 litres of air is

$$\frac{13}{10^5} \times \frac{10^9}{45} \times 10^3 \text{ ppb} = 2.9 \text{ ppb}$$

It has not been possible in the present research to determine the true detection limit of hydrogen sulphide using the methylene-blue colorimetric method owing to practical difficulties. The rapid oxidation of hydrogen sulphide in air and the low boiling point (-60.7°C) cause problems using permeation tubes of the same type as those employed for sulphur dioxide. The problem of oxidation could, however, have been eliminated to some extent by using an inert gas sweeping over the tube. The smallest observable absorbance reading on the spectrophotometer gives a concentration of 0.05 μg hydrogen sulphide in the final solution, which is equivalent to about 3.5 ppb in a 10 litres sample, assuming 100% efficiency (Fig. 4.11). The method may find application as a tool in the detection of hydrogen sulphide in the lower ppb range.

4.2.3.3 Tests with the sulphide-ion selective electrode

Some trials were carried out using a sulphide-ion selective electrode because of the high theoretical limit of

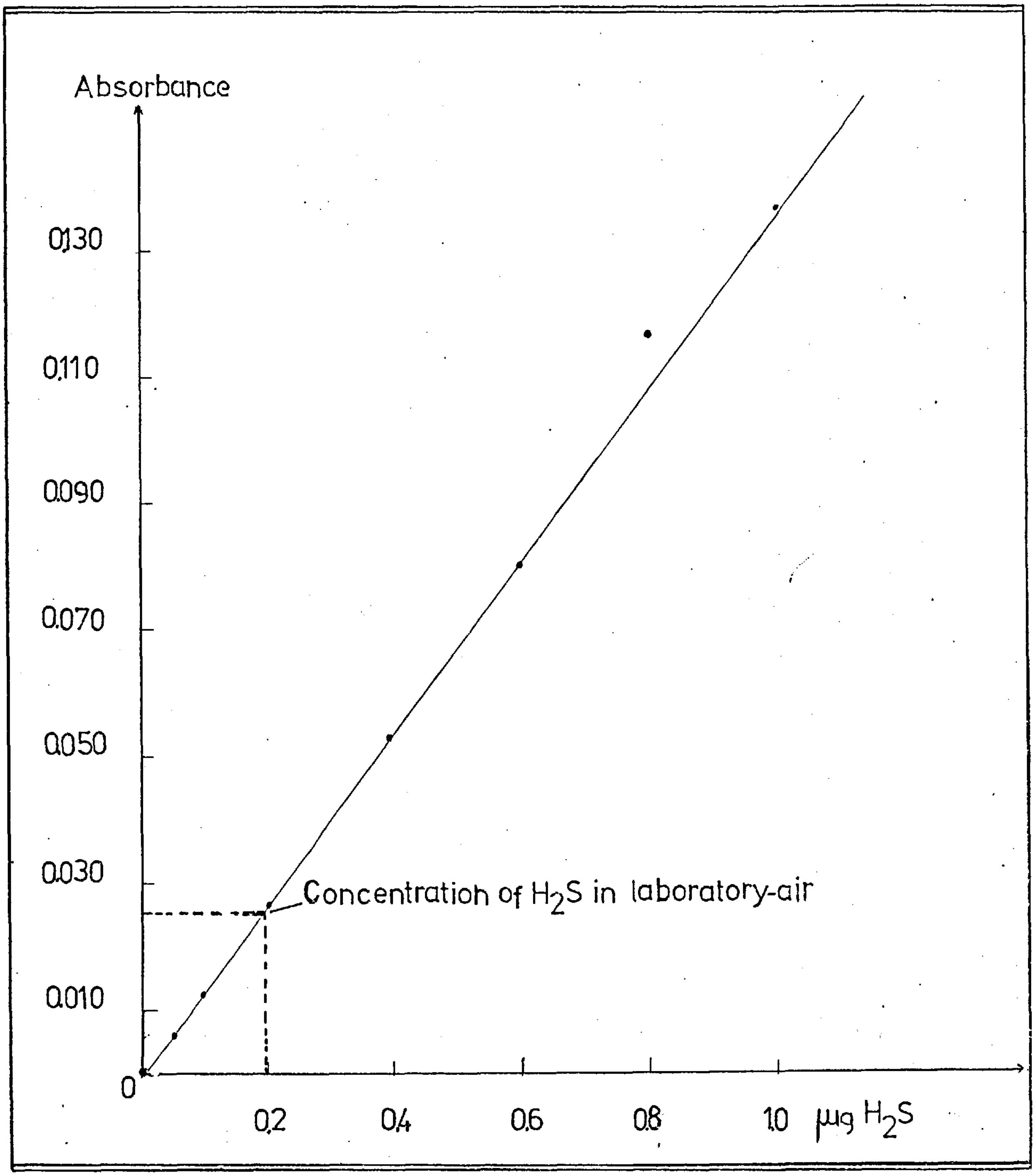

Fig. 4.11 Calibration curve for hydrogen sulphide (Absorbances measured on a Gilford spectrophotometer).

detection (10^{-25}g/ℓ) and proclaimed simplicity and rapidity. These factors contributed to the belief that this method might be useful as a tool in the analysis of trace quantities of hydrogen sulphide, presumed to be present in the soil atmosphere above concealed sulphide-bearing deposits.

However, the method was abandoned due to lack of reproducibility and problems with drift for the low concentrations used, zeroing of the instrument and long response time.

The theory of the sulphide-ion selective electrode was given in Section 3.2.3. A brief summary of the work done and the results obtained is presented below.

All measurements were made with the two reference electrodes illustrated in Fig. 4.12, an Orion Model 407 specific ion-meter, a microvoltmeter and Teflon or glas containers for sample solutions.

In both reference electrodes a porous ceramic separates a saturated nitrate solution from the sample solution. In Fig. 4.12B, the electrode has been equipped with a saltbridge consisting of 3.5M potassium chloride and saturated silver chloride. The saltbridge allows ions to move from one container to the other maintaining neutrality in the solutions by transport of ions. The silver wire cannot come into contact with the sample solution in which the electrode is immersed. All chemicals were reagent grade, used without further purification. A calibration curve was prepared following the procedure described below.

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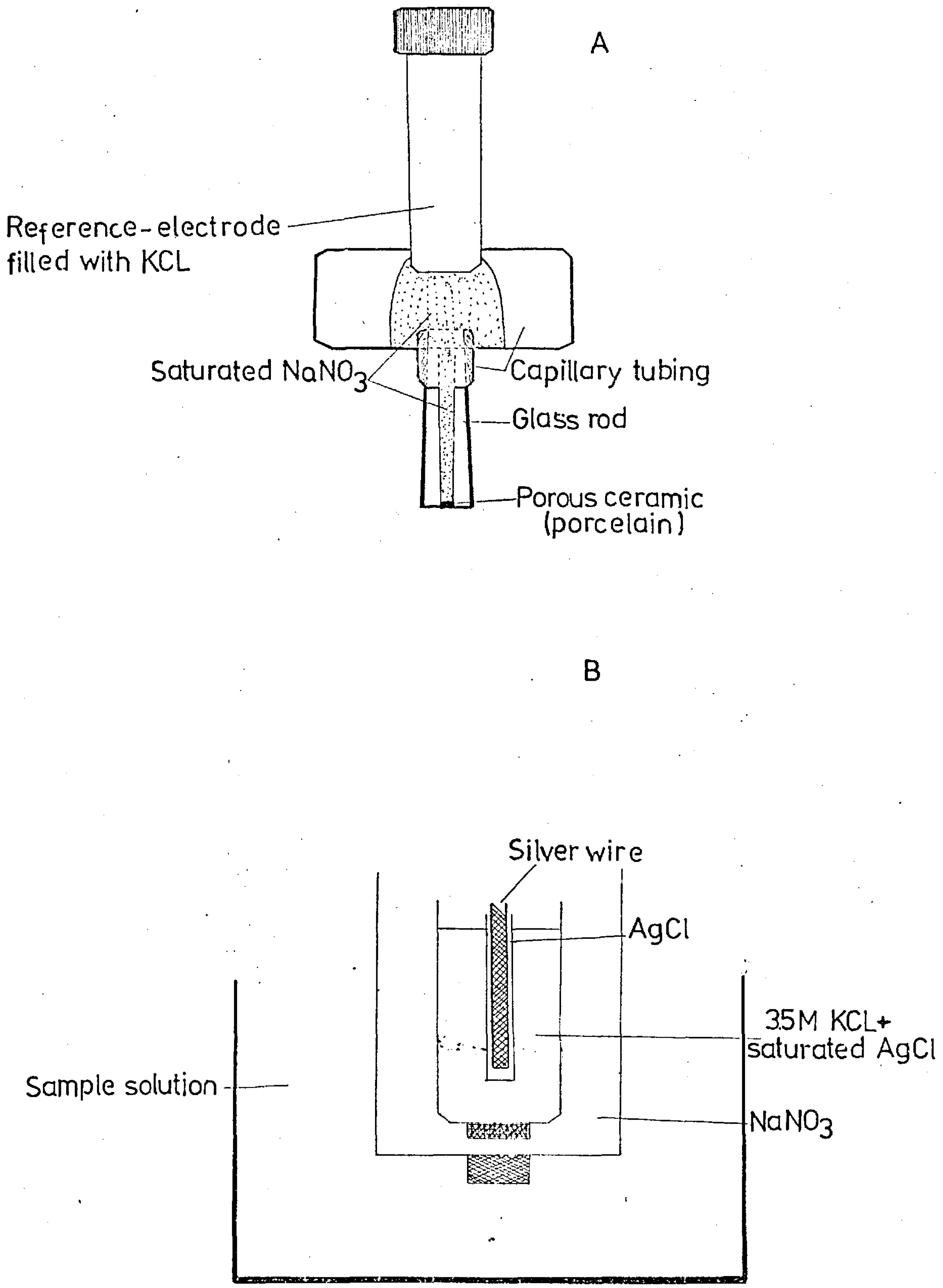

Fig. 4.12 Specific sulphide-ion electrodes

Stock solutions of 1 μg/ml and 10 μg/ml sulphide were prepared daily by direct weighing of hydrous sodium sulphide, followed by dilution in nitrite-free deionized water. A series of standard solutions of sodium sulphide was prepared by suitable dilution of the stock solution. The strength of the stronger sodium sulphide solution was determined following the procedure described on p.83. The ionic strength was kept constant in the test solution by addition of appropriate volumes of buffer solution, resulting in the elimination of many errors. In the ppb concentration level, adsorption and oxidation of sulphide caused serious problems. Arabino-galactan was found useless in the tests carried out due to interference of probable complex formation on the electrode surface.

The selective sulphide-ion electrode was immersed in the Teflon or glass container with a Teflon-coated magnetic stirring bar. Standards of freshly prepared sulphide solutions were added, followed by the addition of buffer solution and other solutions. Cadmium hydroxide suspension was used to absorb the sulphide, followed by its release into solution using acid. Potentials were measured 3 minutes after immersion of the indicating-reference electrode pair into the test solution. The electrodes were carefully washed in 10^{-5} M silver nitrate three times and rinsed with deionized water between readings. The electrode potential exhibited serious drift and non-reproducibility regardless of the type of absorbing solution and strength of the sulphide solution used.

The following reagents were used in the experiment. Aliquots of 0.25, 0.50, 0.75 and 1 ml of ~ 10 μg/ml sulphide solution were added to 2 ml absorption solution of 1 ml each of cadmium sulphate (8.6g/ℓ) and sodium hydroxide (0.6g/ℓ), followed by addition of 1 ml pH 4.6 buffer solution (acetic acid and NaAc) and 1 or 5 ml of silver nitrate (0.05 mg/ml) and sodium nitrate (0.5 mg/ml) solution. The test solution were made up to 25 ml with nitrite-free deionized water. The sodium nitrate ionic buffer was added since acetic acetate buffer alone may interfere. A non-linear response of concentrations below 30 ppb was noticed. Increasing sulphide concentration improved the linearity (Fig. 4.13). Other absorbing solutions such as 0.2M sodium hydroxide were used without improvement, followed by tests with 0.2M sodium hydroxide plus 0.2M ascorbic acid and 2M sodium hydroxide with 5% salicic acid. Ascorbic acid and salicic acid were used as antioxidants.

Afterwards, calibration tests were carried out by adding aliquots of hydrogen sulphide e.g. to the absorbing solutions, followed by measurement of the potential. The small increase in volume for each addition was corrected by the V/v+V factor, when the sulphide solution was added stepwise to the same absorbing solution. All tests were soon interrupted due to problems with drift and non-reproducibility in the lower ppb-concentration range.

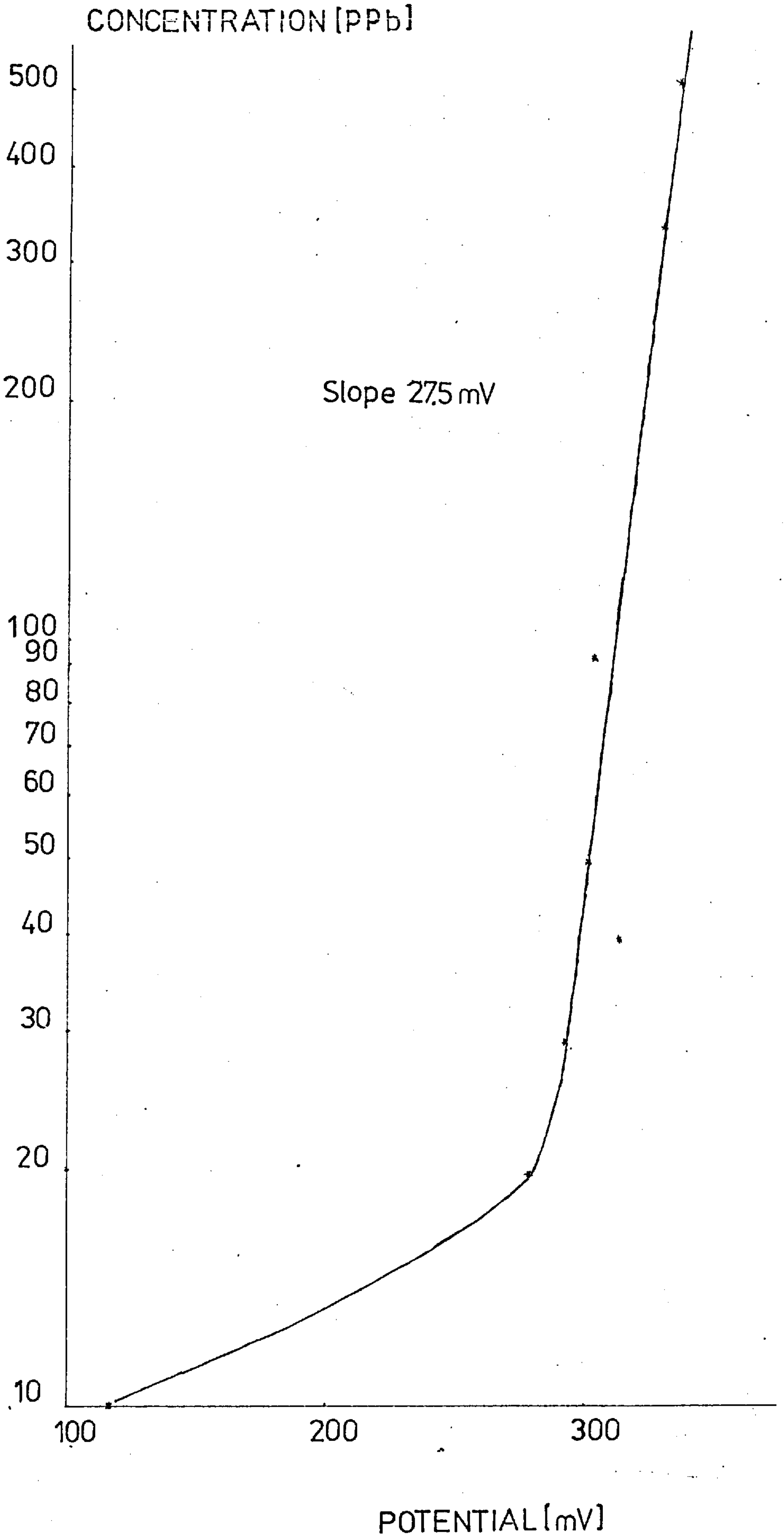

Fig. 4.13 Calibration curve for the sulphide-ion selective electrode. (The curve gives a slope within 2.08 mV of the 29.58 mV per activity decade of sulphide predicted by the Nernst equation at 25^{o}C).

CHAPTER 5

FIELD APPLICATIONS AND DISCUSSION OF RESULTS

5.1 Sampling Techniques

Many techniques may be applied in the sampling and separation of sulphur gases and vapours. In mineral exploration, a few suggestions have been made by Russian investigators such as Kulikova (1960), Ovchinnikov et al (1972) and Shipulin et al (1973), who used drillcores and muds as well as the subsurface atmosphere in their tests determining the gas composition of the soil air. Air displacement, condensation traps, plastic bags, adsorption tubes and gas scrubbers may be used. The two last-mentioned methods have been employed in the present research and will be considered below. Adsorption tubes have been used in conjunction with the gas chromatographic technique and will therefore be described in that section.

In the fieldwork, which was carried out in Great Britain and Spain, the soil air as well as the free atmosphere were sampled and analysed for hydrogen sulphide and sulphur dioxide, using the colorimetric procedures previously described.

The sampling apparatus is illustrated in Fig. 5.1. Two different kinds of augers were used to suit soil type and environment. In Great Britain, the most suitable tool was a 1.3m long, 1.5cm diameter hollow, stainless steel auger, in which two holes had been drilled near the tip, through which the soil gas entered the sampling apparatus. Depths of 30 - 40cm were rapidly and easily reached. This tool was

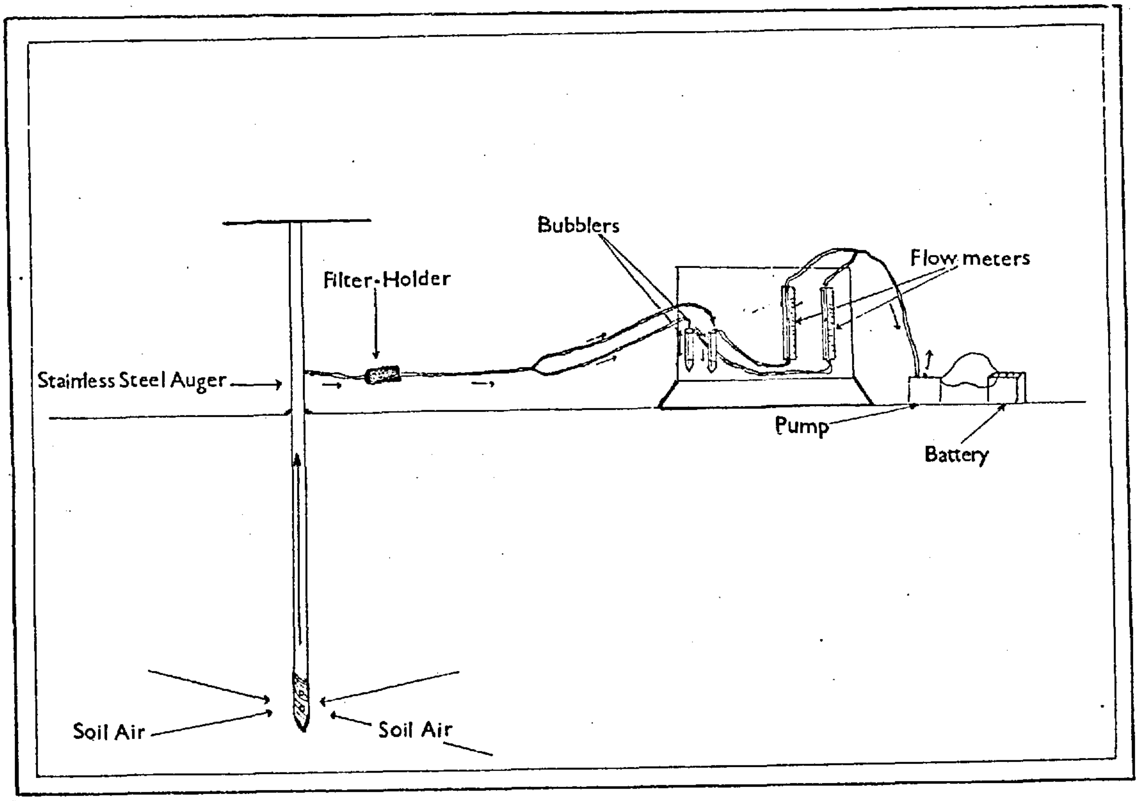

Fig. 5.1 Soil air sampling apparatus

found to be very impractical in the hard and stony soils of S.E. Spain. Depths of 10 - 15 cm were reached only with difficulty. A steelprobe, as illustrated in Fig. 5.2, was made and used in the semi-arid soils of S.E. Spain. The probe consists of two parts, a removable internal steel rod and a hollow, external steel tube. After hammering the probe 30 - 35cm into the soil with a sledge-hammer, the internal rod was removed and the steel tube sealed with a cap, through which a pvc tube was led. The soil air entered the sampling system through several holes near the end of the tube. Difficulties with this probe arised, when the probe had to be removed after sampling, since it became jammed easily whilst in the ground. Another drawback was the welded head on the rod which was easily broken, when the sledge-hammer hit the probe.

A glass-fibre dust filter, held in a plastic holder, was used to prevent particles from entering the absorbing solutions for sulphur dioxide and hydrogen sulphide. All connections were made of pvc and glass.

The holes near the end of the auger or the probe were cleaned from soil particles by blowing air into the hollow stem with a hand rubber bellow. The edges between the soil and tool were sealed with debris to prevent atmospheric gases to enter the sampling system. The subsurface atmosphere was drawn into the sampling system with the aid of a Capex Mark 2 suction pump powered by a 12V car battery. The air-stream was split into two after passing the dust-filter. After bubbling through the tetrachloromercurate absorbing solution for sulphur dioxide and the cadmium hydroxide absorbing solution

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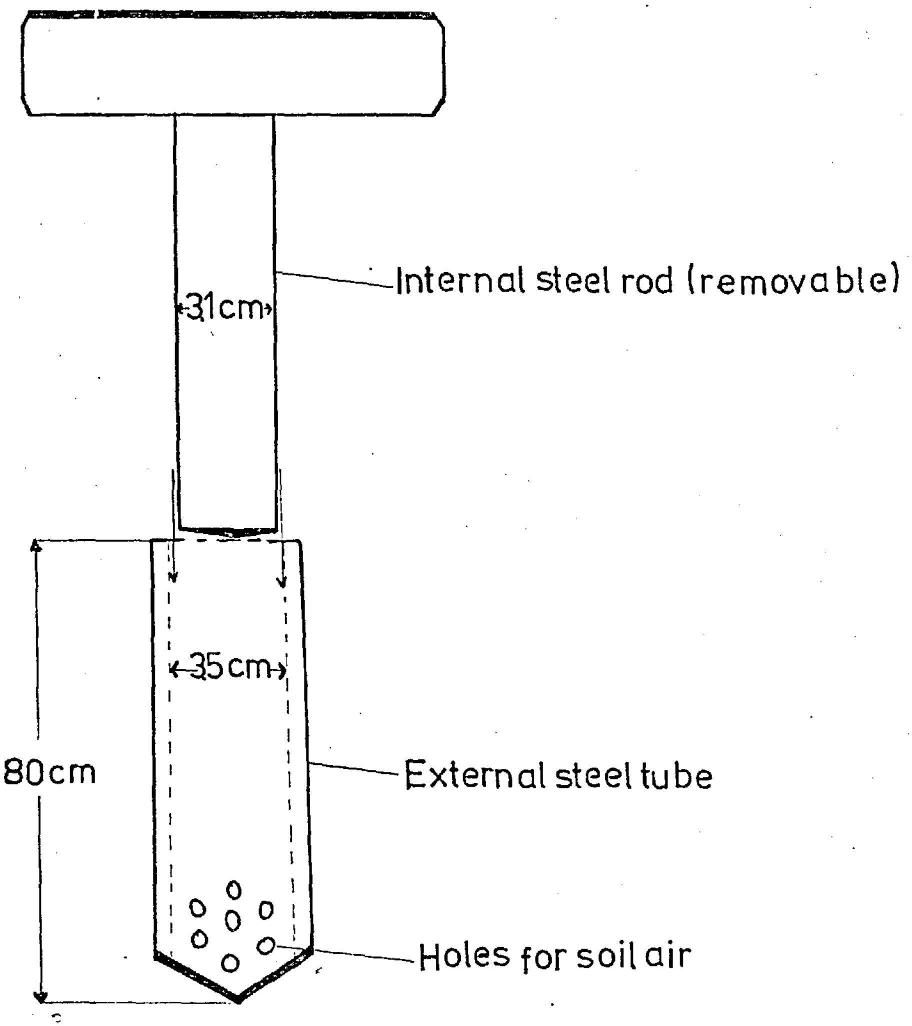


Fig. 5.2 Hammer-probe

for hydrogen sulphide, the two air-streams were reconnected. The flow-rates were controlled with two adjustable air-meters installed in the system directly after the scrubbers. After sampling, the scrubbers were removed, sealed and stored in a cold-box with ordinary ice until analysis.

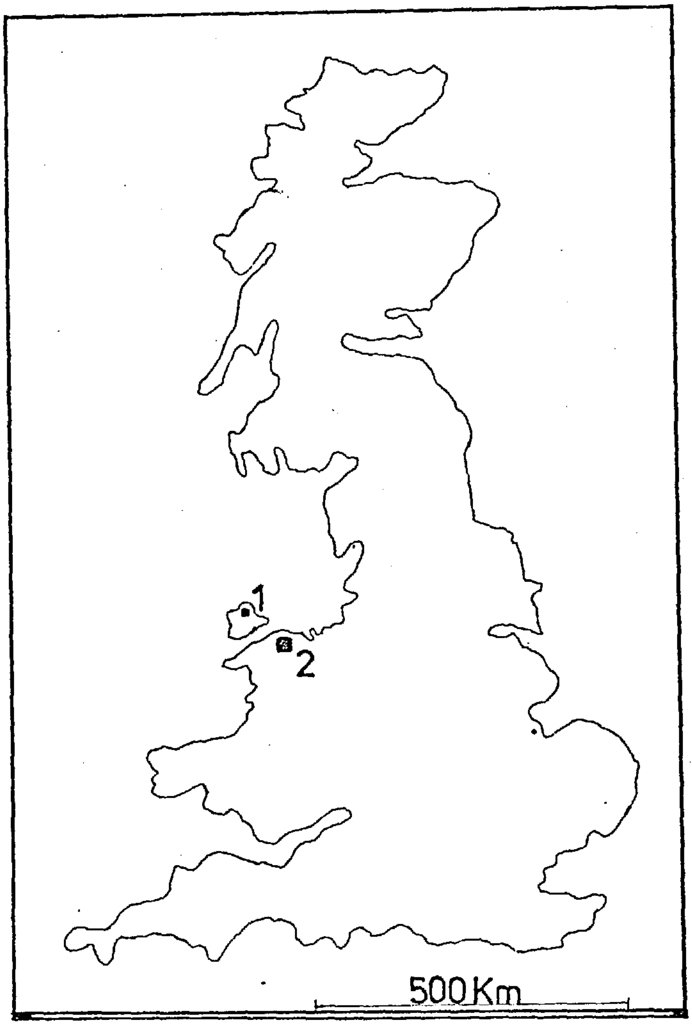
5.2 Description of Fieldareas and Fieldwork in Great Britain

Four survey areas were selected for the project. Two of these are situated in northwest Wales (Figs. 5.3 - 5.4). The geology and mineralization of the individual areas are described below.

5.2.1 Trefriw

The area is situated near a disused mine on the western slope of the Conway valley, about 1.6 km north of Trefriw village. The highest summits of the hills in the surroundings of the old workings reach about 280m above the river. The hillside is covered with a forest of hazel and birch. North of the mineralization, pine is the dominant species. The ground surface is seldom exposed to the sun owing to the vegetation. A large number of dumps and screes of sulphide-rich boulders are found outside and down the hillside, east of the shafts.

The geology of the area has been described by Sherlock (1918) and is illustrated in Fig. 5.5. The pyrite-rich ore occurs in a slightly folded vein, that runs up the hillside. Sedimentary cleaved rocks, consisting entirely of shales are separated in the south from an intrusive diabase and in the



1. Parys Mountain

2. Trefriw

Fig. 5.3 Location of fieldareas in Great Britain

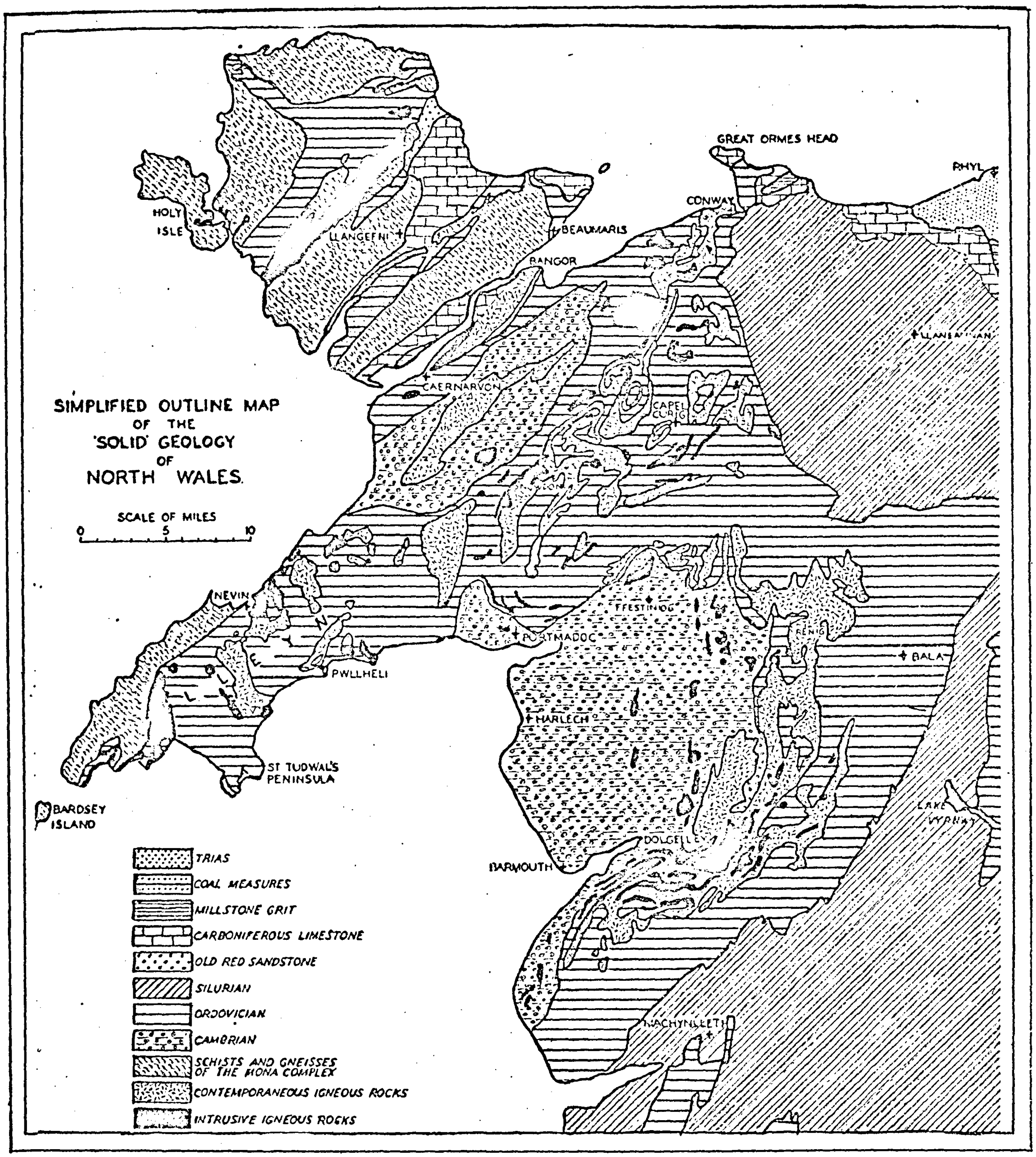


Fig. 5.4 The geology of north Wales (after Smith and Neville, 1935).

Map and section, on identical scales, of the Trefriw pyrites deposit.

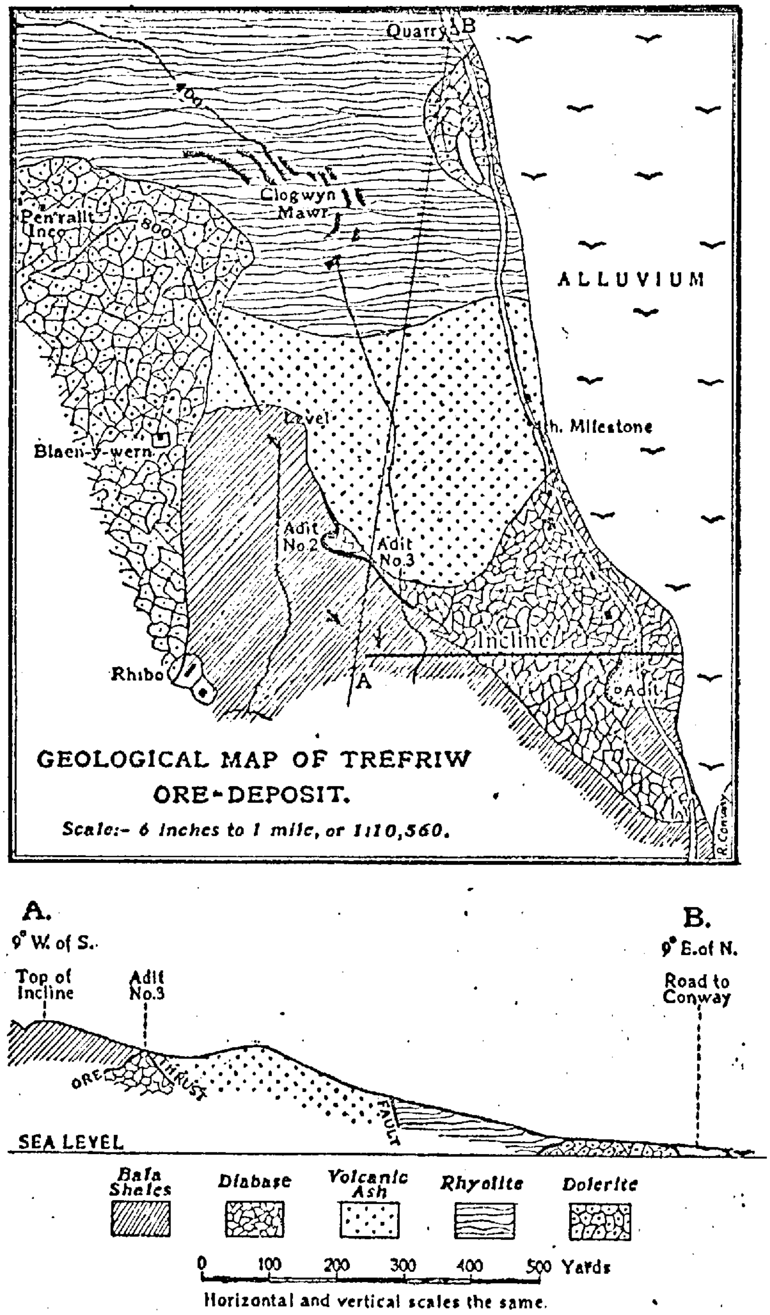


Fig. 5.5 The geology of Trefriw pyrite ore deposit (after Sherlock, 1918).

north from volcanic ash by the mineralization. Metamorphism of the rocks is weak. Contact alteration is noticed in that the shales have hardened and contain crystals of pyrite. The base of the intrusive is exposed in an adit close to the road. When proceeding northwards, the geology changes from volcanic ash to a dark-grey, fine-grained rhyolite. Overlying these rocks, on top of the hill the bedrock consists of dolerite, which is also found close to the road in northeast.

Sherlock regards the mineralization to be of sedimentary origin by comparing the occurrence of ore with other deposits and geological strata in north Wales. He concludes, that the pyrite has been formed from iron-ore and the influence of heated water, derived from the intrusion. Figs. 5.6 - 5.9 illustrate the concentrations of Cu, Fe, Pb and Zn in the topsoil at Trefriw. No surficial expression of the mineralization is indicated by these elements. The soil samples were initially dried at $60^{o}C$ for 15 hours. After sieving the samples, using an 80-mesh (c. 200 μ) nylon sieve, 0.250g of the undersize was weighed and attacked with 5 ml of 4:1 nitric acid/perchloric acid to dryness. The residue was then bleached with 2 ml 5M hydrochloric acid. The samples were then placed on a hot plate for 2 hours, followed by dilution to 10 ml with deionized water. The elements were finally determined by atomic absorption spectrometry.

5.2.2 Parys Mountain

The fieldarea is located on the plateau of Parys Mountain in the northern part of Anglesey, about 2.5 km south of Amlwch. The hill is about 160m above sea level and is

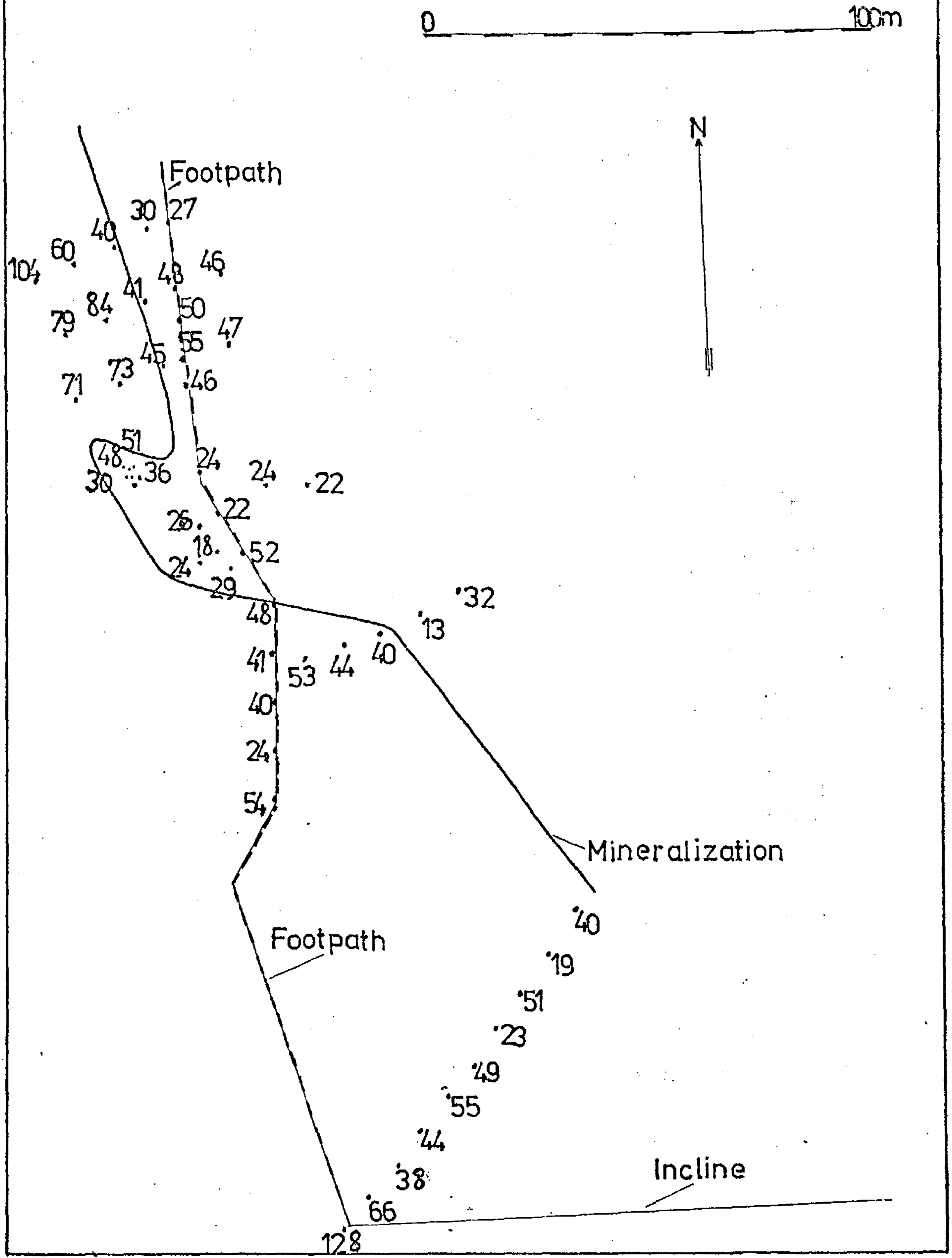


Fig. 5.6 Distribution of Cu (ppm) in the topsoil at the Trefriw sulphide deposit.

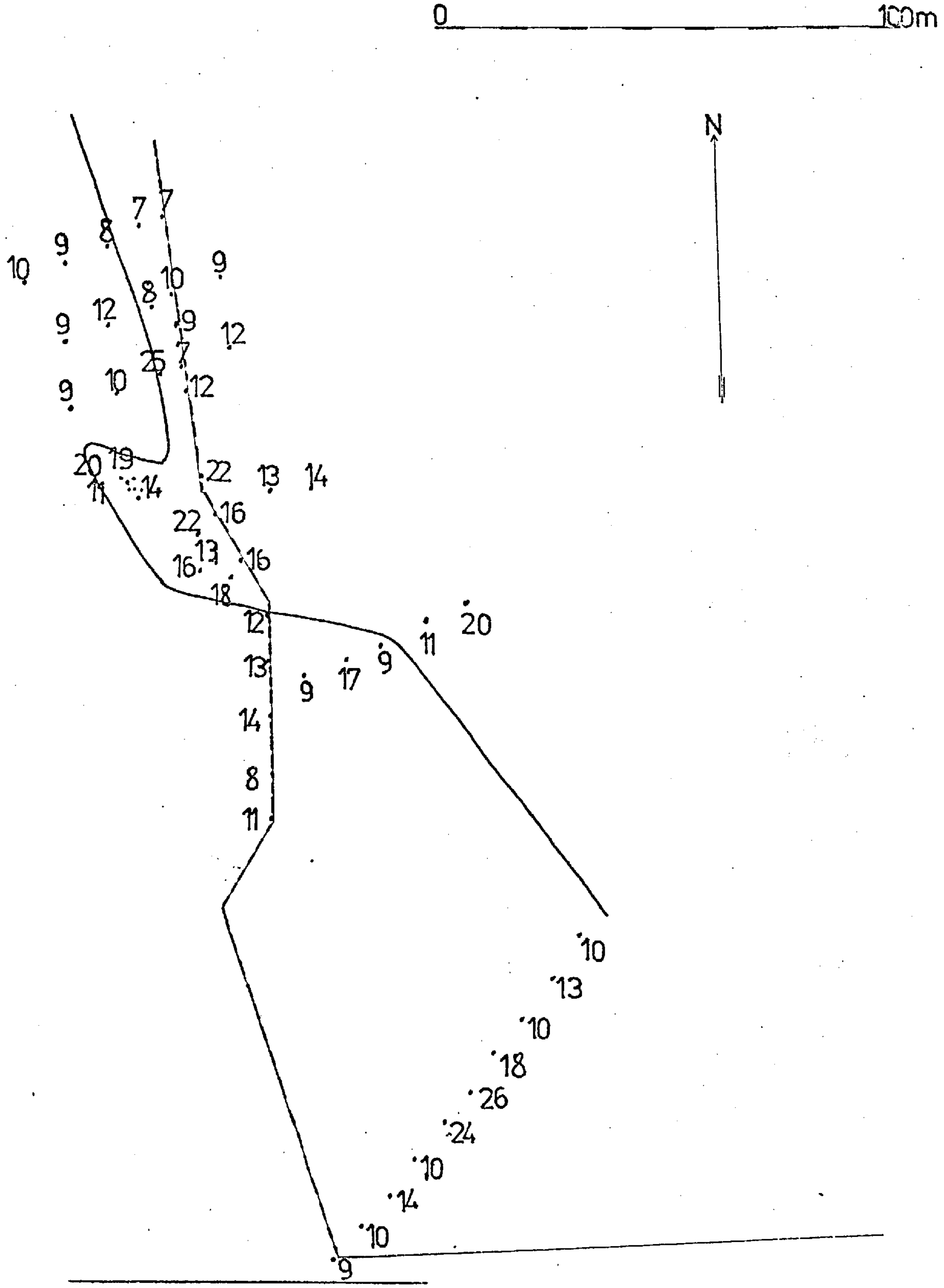


Fig. 5.7 Distribution of Fe (%) in the topsoil at the Trefriw sulphide deposit.

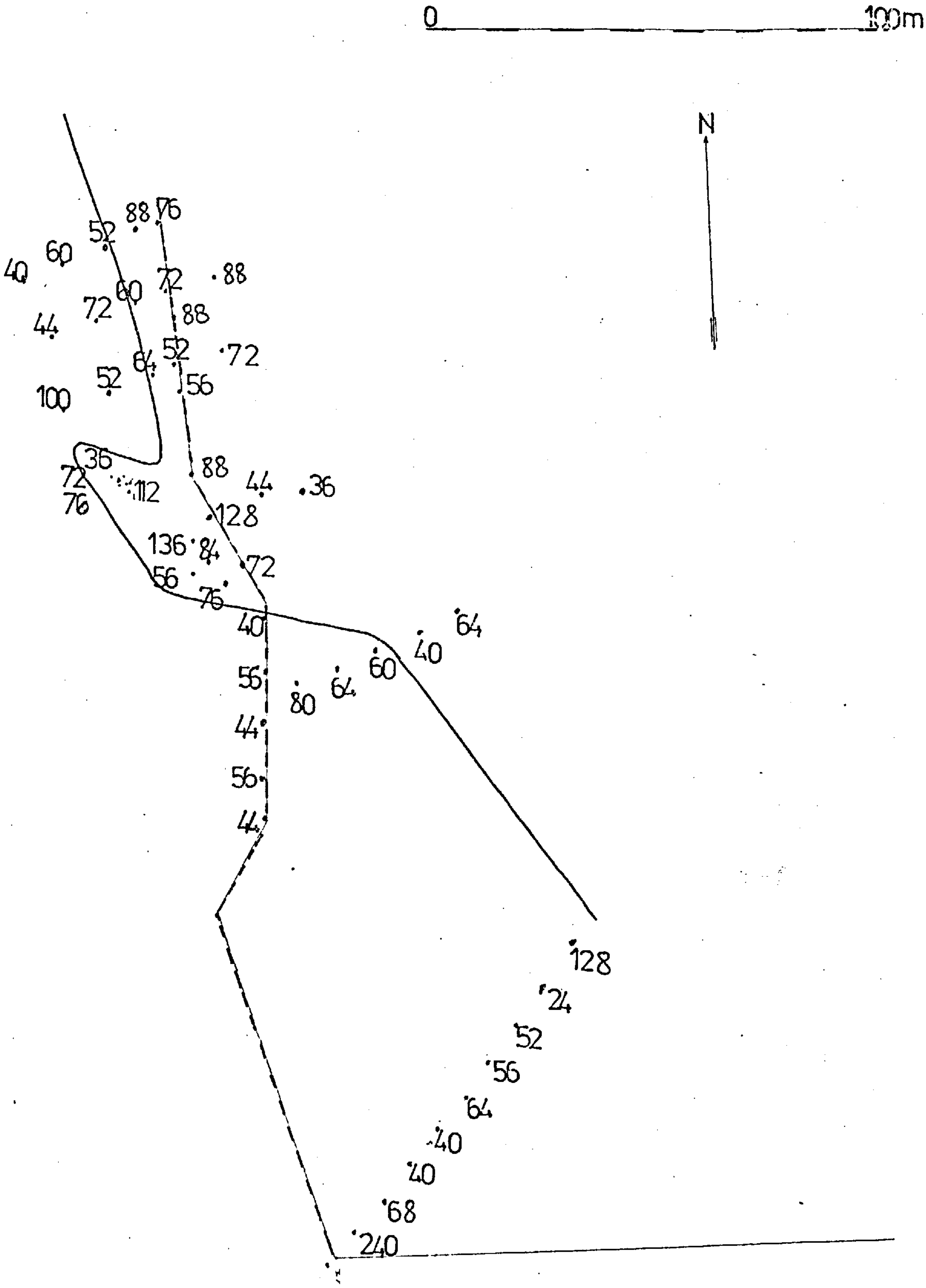


Fig. 5.8 Distribution of Pb (ppm) in the topsoil at the Trefriw sulphide deposit.

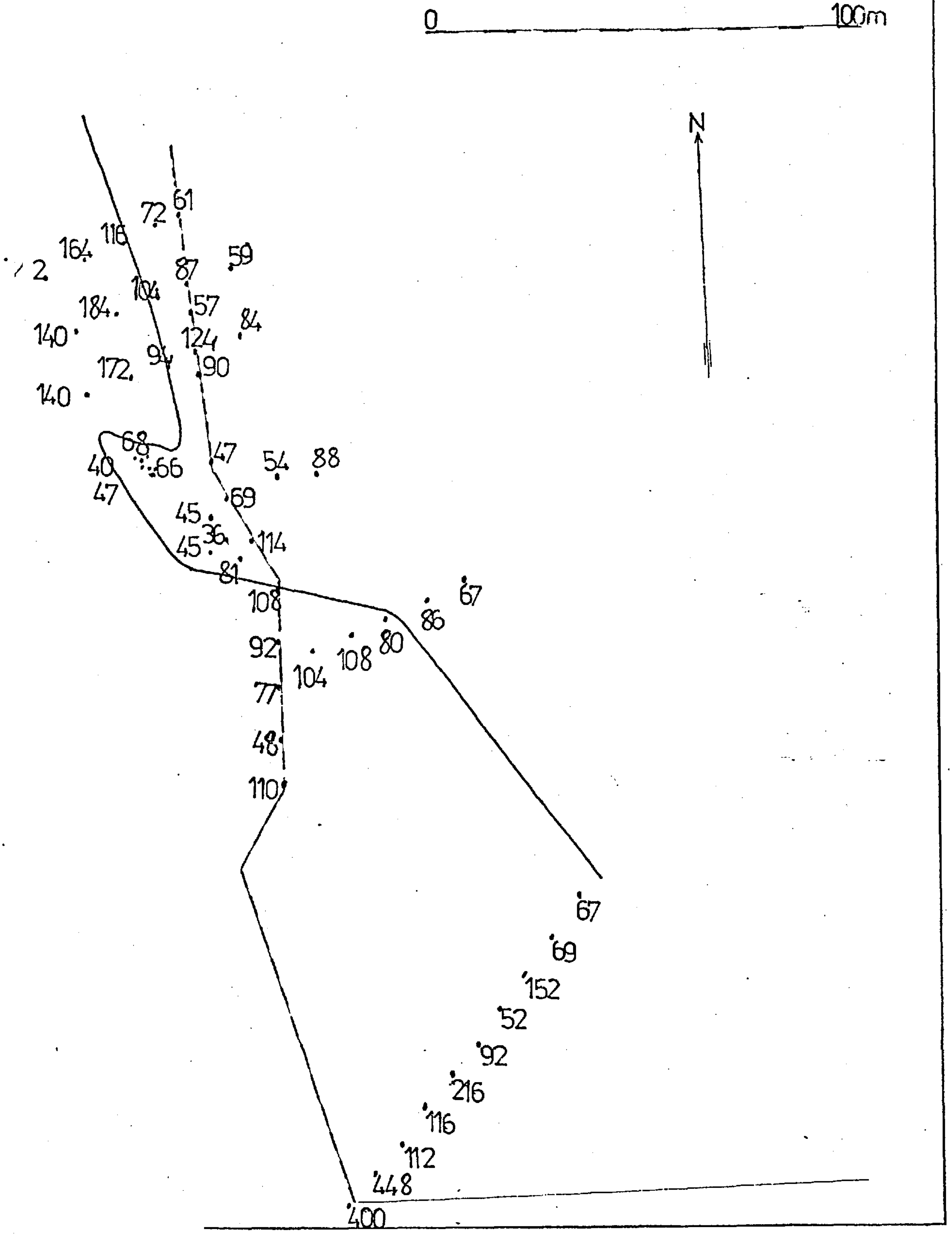


Fig. 5.9 Distribution of Zn (ppm) in the topsoil at the Trefriw sulphide deposit.

elongated for about 2.5 km in an E-N-E direction. Mining activities started in 1768 and ended at the end of the last century (Hawkins, 1966). Until recently, (1964) copper was extracted in precipitation pits near the old mines. Sulphate-containing water was led into these basins and allowed to react with iron scrap dumped into the pits. Copper and ferric oxide precipitated. The higher and central parts consist of dumps and two major pits, about 30m in depth. The weathering of sulphides has produced sulphuric acid resulting in a barren surface almost without vegetation. Sulphide-rich boulders are found everywhere and iron-stained rocks are frequently exposed. A stronger colour alteration, from green to brown-red and violet, is characteristic of the whole area. In the rocks, especially in the western pit, sulphides (pyrite and some oxidized copper minerals are abundant).

The geology of Parys Mountain has been described by Greenly (1919) and Hawkins (1966). From north to south, the following sequence of rock types is encountered (Fig. 5.10): Precambrian rocks (Mona complex), Ordovician shales (Parys shales), vein quartz, acid volcanic rocks and sediments (felsite) and Silurian shales (Llandovery shales). In both types of shale, basic intrusions of dark-green dolerites frequently occur.

All rocks on Parys Mountain have been metamorphosed to varying extents and have undergone various degrees of mineralization, micasization and silicification.

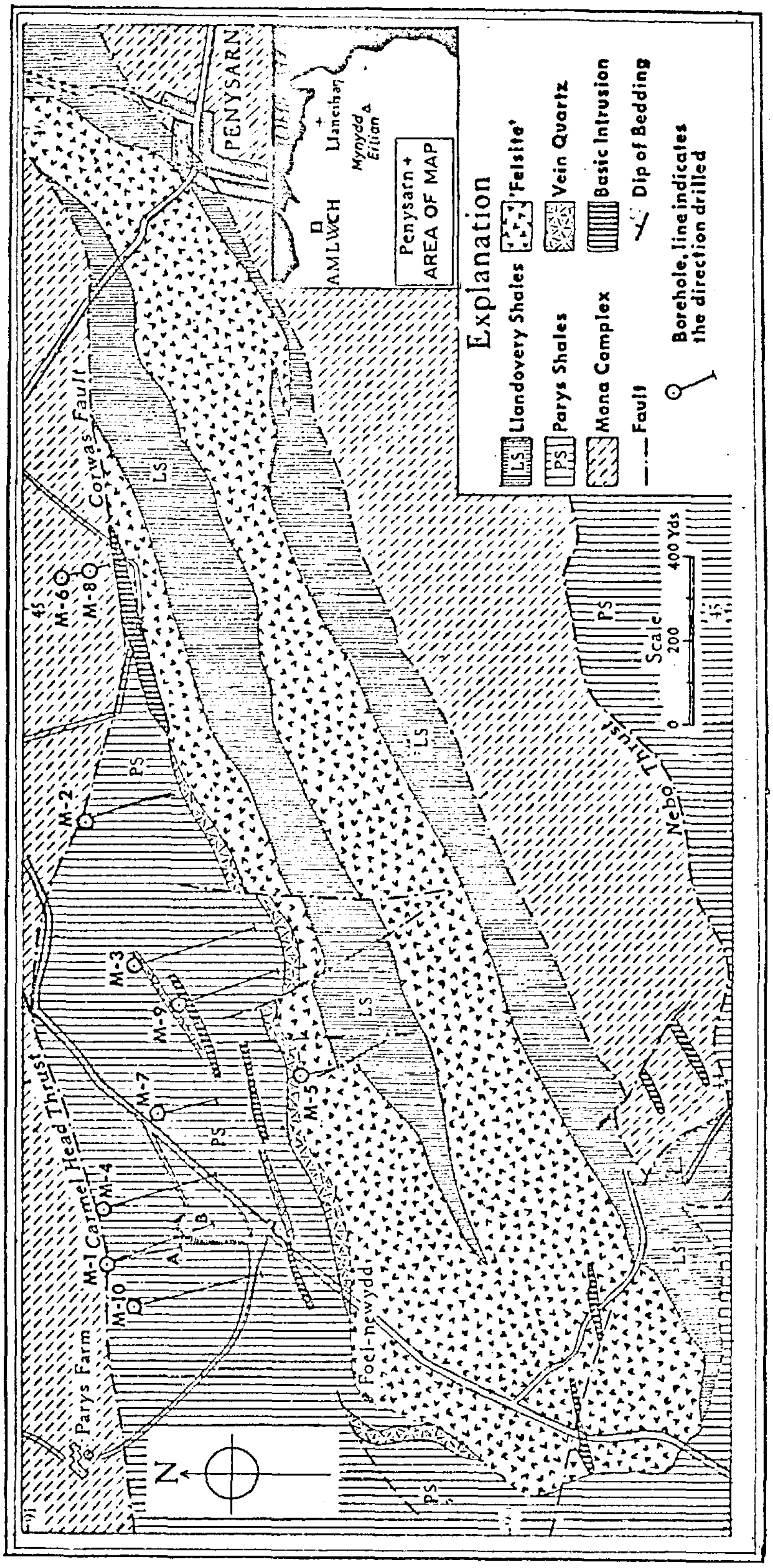


Fig. 5.10 Geology of Parys Mountain (after Hawkins, 1966).

Hawkins description of the geology of Parys Mountain is based on results from a drilling programme, which was undertaken at the beginning of the 1960's. The drillcores indicate three subdivisions of the Ordovician shales: (1) shales with sedimentary breccia beds, (2) grey shales with numerous sulphide-rich quartz veins (weather to brown and green colour) and (3) black shales with scattered pyrite crystals.

Greenly (1919) called the compact and homogeneous acid volcanic rocks "felsite". He considered that the felsite was intruded into the Ordovician and Silurian shales, but Hawkins (1966) found that the felsite consists of three distinct rock types: (1) rhyolite, (2) altered sediments (mudstones) and (3) tuffs.

The felsite seems to be folded into a large isoclinal fold, enclosing the Silurian shales in the core. The latter dip about 50° to northeast, and are well exposed in the workings of the old mine. The Silurian shales reappear in the south and seem to form a complementary anticlinal with felsite in its core. The Ordovician shales near the summit of the hill are hardened and full of secondary quartz.

Pyrite is found as veins and disseminations of varying intensities and is associated with galena, sphalerite and chalcopyrite.

5.2.3 Fieldwork

In June 1975, fieldwork was carried out at the sulphide deposits at Trefriw and Parys Mountain with the objective of testing the two colorimetric methods for sulphur dioxide and hydrogen sulphide in in situ measurements under field conditions. Necessary chemicals and an SP600 spectrophotometer were taken to the field together with the sampling device, which has been described above. Solutions were prepared at Bangor University, where the measurements of absorbances were also carried out.

Absorbing solutions were prepared indoors and transported in a cold-box with ordinary ice to the field. The scrubber for hydrogen sulphide was permanently protected from light. The sampling procedure and apparatus employed have been described elsewhere. At all sampling sites, 15ℓ of air were sampled. Sampling time and flow-rate were varied and the results compared.

The soil atmosphere as well as the atmosphere just above the ground were sampled at both localities. At Trefriw, samples were taken from a depth of 20 - 40 cm, while at Parys Mountain, the samples were collected at a depth of 15 - 25 cm as an abundance of boulders and stones in the ground prevented deeper sampling. In both areas, the characteristic smell of weathering sulphides was noticeable. The odour was most intensive at the entrance to the main adit, marked as adit no. 2 on the geological map of Trefriw by Sherlock (Fig. 5.5), but it also could be recognized close to the sun-exposed dumps in both areas. At the Trefriw deposit, the surface of the ground was shaded by dense vegetation. Only a few areas of scree on the hillside were exposed to the sun.

In the absorbance measurements, which were carried out each evening, as soon as possible after collecting the samples, it soon became evident that hydrogen sulphide could not be detected, and that sulphur dioxide was only found in samples from the Trefriw area. The highest concentrations were obtained in samples from the main adit, where the odour was most intense (Table 5.1). Fig. 5.11 shows a calibration curve for sulphur dioxide used in the calculations of sulphur dioxide concentrations. A test of samples from the same sites on another day gave figures on the absorbances in the range of the blanks.

Table 5.1 Concentrations of sulphur dioxide in soil air, and atmosphere at the Trefriw pyrite ore deposit

Sample	Time (min)	Flow-rate (ℓ/min)	Volume (ℓ)	Concentration (ppb)
Adit soil air (sulphide-rich soil)	30	0.5	15	15.3
Adit air	30	0.5	15	12.6
Adit air	15	1.0	15	6.1
Scree soil air	30	0.5	15	0
Air above scree	30	0.5	15	5.7

The sulphur dioxide concentration was calculated from the formula:

$$C = 5 \times \frac{a}{V} \times 0.382 \text{ (in ppm)}$$

C = concentration

a = concentration in μg of SO_2 in 1 ml solution (in 5 ml solution, there is

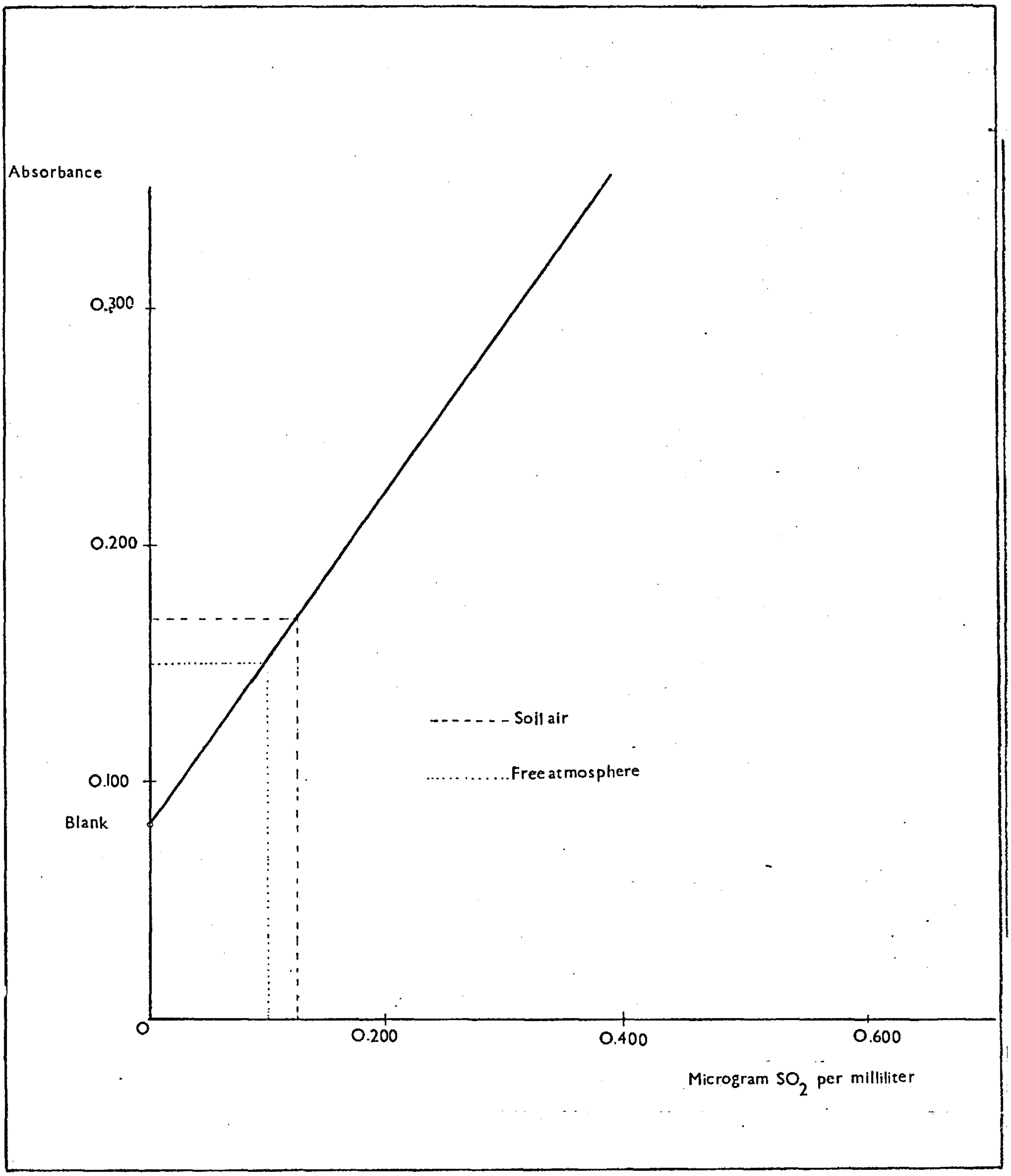


Fig. 5.11 Calibration curve for SO_2

5 x a μg SO_2)

0.382 = The volume ($\mu \ell$) of 1 μg SO_2 at 25°C, 760mmHg

V = Sample volume in litres

5.3 Description of Fieldareas and Fieldwork in Spain

The lack of positive results from Wales were ascribed to damp conditions and low environmental temperatures. Therefore, fieldwork utilizing the West-Gaeke and the methylene-blue colorimetric methods for the detection of sulphur dioxide and hydrogen sulphide respectively was carried out in July, 1975, in the semi-arid region of southeast Spain. By including this relatively arid region, many parameters such as influence of precipitation, soil moisture content and vegetation etc. could be neglected. These variables were important in the British areas. A description of the two Spanish fieldareas and fieldwork carried out is presented below. Fig. 5.12 shows the volcanic region of Cabo de Gata, where the fieldwork was carried out near Rodalquilar and San Josè.

5.3.1 Rodalquilar

The fieldarea is located in close vicinity of Minàs Rodalquilar in southeast Spain. The surroundings of the mining village are characterized by mountains and valleys with old cultivated fields on alluvial and colluvial deposits. An abundance of quarries and dumps reveals an intensive previous mining activity, that ended only a decade ago. Vegetation is

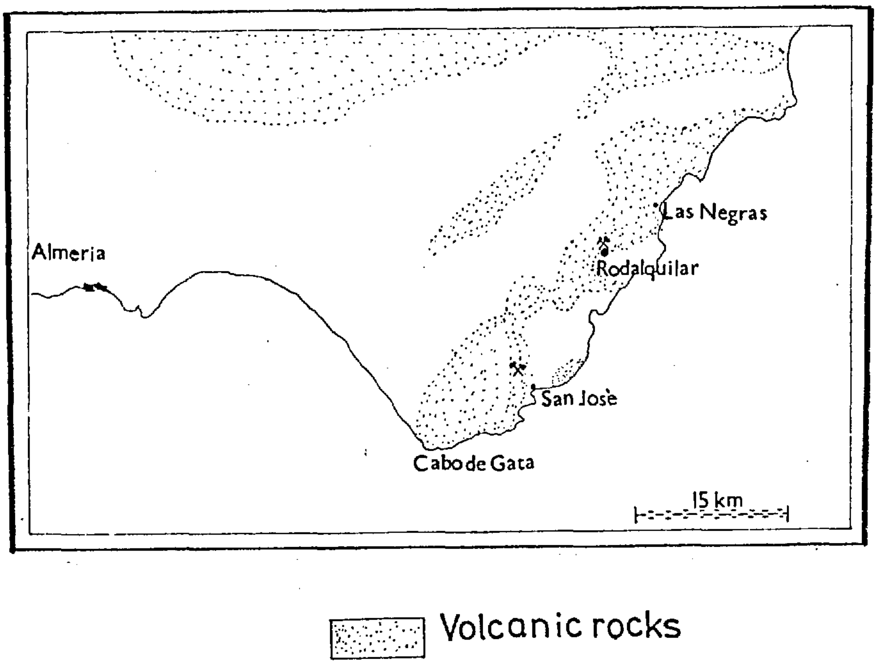


Fig. 5.12 The volcanic region of Cabo de Gata (after Martin-Vivaldi, 1963).

sparse and consists mainly of low-growing thorny shrubs and some grass. Numerous yellow to light-green sulphur-rich dumps are dispersed throughout the whole district and many have the odour of oxidizing sulphides. The waste tips are well exposed to the sun and were considered to be suitable for a preliminary test of the sampling techniques. A weak sea-breeze cools the lower atmosphere, but the surface of the ground gets very hot during summer days, resulting in a dry and cement-hard topsoil. Accumulations of gypsum and alunite occur frequently in the whole region. In the dumps, pyrite and oxidized copper minerals are found.

The general geology of the volcanic rocks in the Cabo de Gata region has been described by Ossan (1889). Studies on the formation and the occurrences of bentonite and montmorillonite in the area have been made by Martin-Vivaldi (1963). The geology of Rodalquilar is characterized by strongly calc-alkaline volcanic rocks, extending in a SW-NE direction. The volcanic bedrock is locally covered by Miocene and Pliocene sediments (Fig. 5.12). The composition of the eruptives is andesitic, dacitic and occasionally also rhyolitic. A common feature of all types is an abundance of 1 cm porphyroblasts of cordierite and almandine as well as of other silicate minerals (Zeck, 1972). Accumulations of bentonite and montmorillonite are found frequently in the area.

The gold-bearing mineralization of Rodalquilar is considered to be of Neogenic age and contemporary with the volcanism. The volcanic rocks have undergone alteration in the zone where the gold mineralization appears. The mineral association is quartz-alunite-pyrite-illite-kaolinite-chlorite. With increasing distance from the mineralization, chlorite becomes more abundant while, on the other hand, alunite and kaolinite tend to be more rare. The gold mineralization appears as breccia fillings and is located in the subvolcanic zones of the volcanic complexes. Pyrite is found in varying amounts in the wall-rock, with minor occurrences of copper sulphides. The zone of a primary sulphide mineralization occurs below 200m from surface (Vivaldi et al, 1971).

5.3.1.1 Fieldwork

Absorbing solutions of potassium tetrachloromercurate (TCM) and cadmium hydroxide were prepared daily indoors and were stored in a cold-box with ordinary ice before and after sampling. The absorbance determinations were carried out in the evenings, some hours after the last in situ sampling.

Initial trials were carried out on the numerous green-yellow sulphide-rich dumps near Rodalquilar. The odour of sulphides could be detected throughout the area. A surface temperature in the range of 28 - 33^{o}C was measured each day. Sample depths varied from 30 to 40 cm. The free atmosphere was also sampled about 70 cm above the ground.

Initially, a number of dumps and tailings were sampled in an attempt to localize a suitable site for further investigations. A pumping rate of 0.5 ℓ/min was used over a sampling time of 20 minutes. Results were discouraging despite the odour in the proximity of the sulphide-rich dumps. Hydrogen sulphide was not detected in any sample and the absorbances of the samples, analysed for sulphur dioxide, were within the range of the blank values.

A sampling rate in the range 0.5 - 7.0 ℓ/min was thereafter tested over a period of 10 to 30 minutes. No variations in the absorbances were measurable.

In the belief that sulphur dioxide was oxidized, 2% arabino-galactan (antioxidant) was added to the tetrachloromercurate absorbing solution to prevent or to inhibit the loss of sulphur dioxide. In the first tests, higher absorbances were achieved in solutions with arabino-galactan as compared with those without. A test of the variation of blank samples under different conditions was carried out as follows:

(1) The absorbances were measured for blanks, with and without arabino-galactan; no differences were observed.

(2) Blanks, with and without arabino-galactan, were taken to the field or kept indoors; a comparison of the absorbances gave similar values.

(3) The different reagent solutions were added with either a 1 ml pipette or an Oxford laboratories 250 ml dispensor; results varied only when adding pararosaniline with a dispensor.

(4) Blanks were stored indoors and outdoors under field-conditions for seven hours; no differences in the absorbances were noticed.

According to the investigation above, the blanks are not affected by the addition of arabino-galactan and a long storage time. It was decided that all solutions should be added with a pipette due to the sensitivity of blank values to concentration of the pararosaniline solution.

The following trials included sampling at a rate of 0.5 ℓ/min during times ranging from 10 to 180 minutes, using absorbing solutions with and without arabino-galactan. The results are shown in Table 5.2.

The sample absorbances differ very little from the blank values, indicating that sulphur dioxide is not apparently present in measurable amounts in the soil atmosphere, using this method.

Table 5.2 Absorbances of soil-air samples in the Rodalquilar fieldarea

Sample	Time (min)	Volume (ℓ)	Arabino-galactan	Absorbance	Time of Day
Blank			-	0.128	
1	10	5	-	0.150	9.30-9.40
2	10	5	+	0.144	"
3	20	10	-	0.128	9.45-10.05
4	20	10	+	0.152	"
5	30	15	-	0.125	10.10-10.40
6	30	15	+	0.152	"
7	30	15	-	0.118	10.40-11.10
8	30	15	+	0.152	"
9	20	10	-	0.132	11.25-11.45
10	20	10	+	0.141	"
11	10	5	-	0.125	11.46-11.56
12	10	5	+	0.143	"
13	10	5	-	0.140	12.00-12.10
14	10	5	+	0.153	"
15	60	30	-	0.134	12.15-13.15
16	60	30	+	0.148	"
17	180	90	-	0.115	13.20-16.20
18	180	90	+	0.175	"
Blank			+	0.130	

In attempts to detect sulphur dioxide, further work was carried out. Samples were brought to the spectrophotometer for analysis immediately after the sampling and were compared with samples kept in the field for some hours. No variation of the absorbances were observed. Two bubblers were thereafter connected in series for efficacy tests giving the results shown in Table 5.3.

Table 5.3 Efficiency tests of the tetrachloromercurate absorbing solution (TCM)

Sample	Flow-rate	Time	Arabino-galactan	Absorbance
1 (1st bubbler)	0.5	20	-	0.305
2	0.5	20	-	0.152
3 (1st bubbler)	0.5	20	+	0.250
4	0.5	20	+	0.180
Blank			-	0.168
Blank			+	0.160

Sulphur dioxide was artificially prepared and dispersed in proximity of the sampling device. The efficiency of the absorbing solution can be considered to be satisfactory, since more than 90% of the gas is absorbed in the first bubbler.

With the objective to detect sulphur dioxide photodecomposition of the tetrachloromercurate solution and oxidation of sulphur dioxide were eliminated by the following modifications: (1) the scrubbers were kept in darkness during the sampling, (2) the samples were stored in a cold-box filled with ordinary ice before and after sampling and (3) the scrubbers were immersed in an ice-bath during sampling. A flow-rate of 0.5 ℓ/min was used over a sampling time of 20 minutes. These modifications gave the results shown in Table 5.4.

Table 5.4 Absorbances measured in soil air samples from Rodalquilar dumps (flow-rate: 0.5 ℓ/min; volume: 10 ℓ)

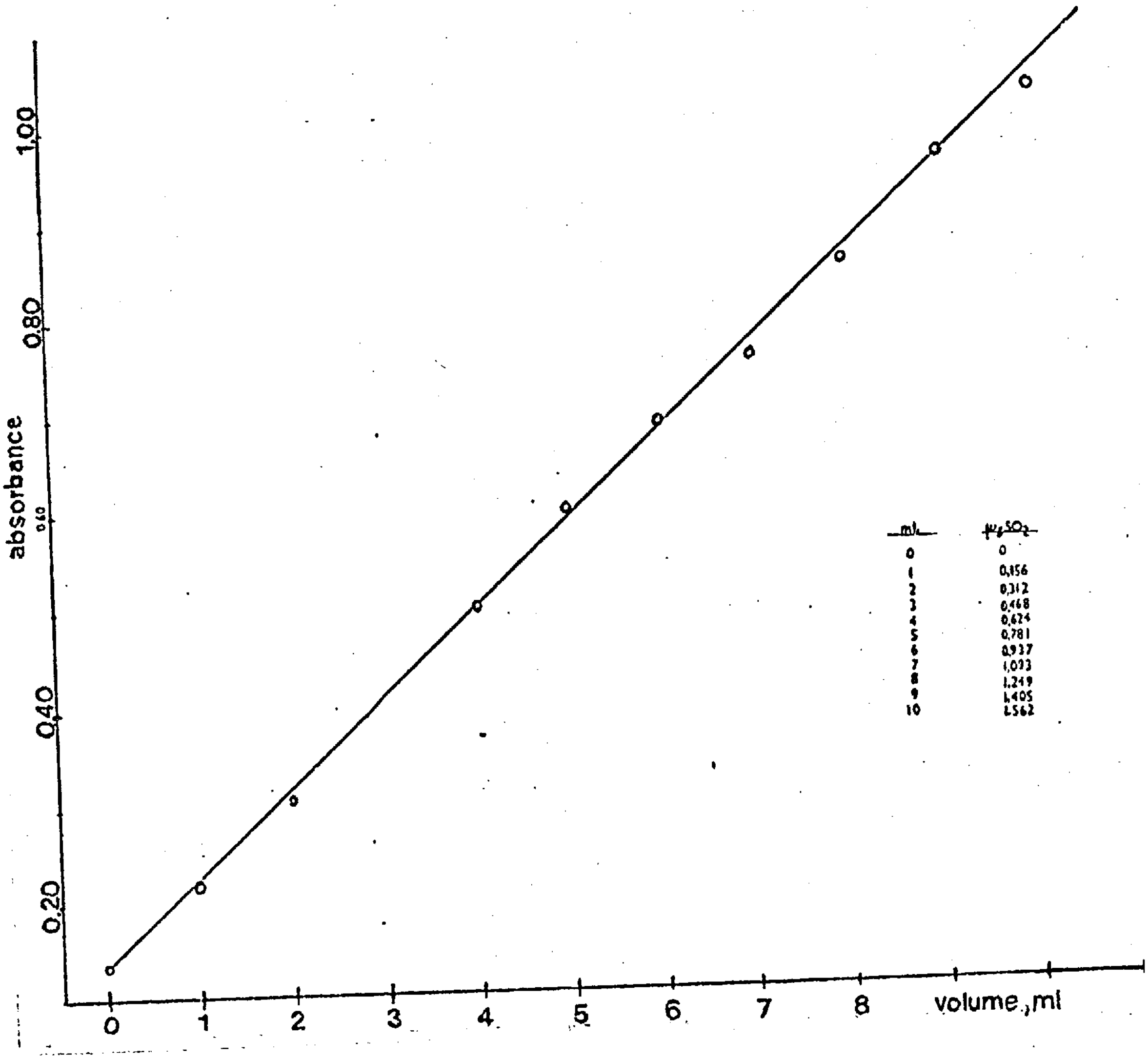
Sample	Arabino-galactan	Ice-bath	Absorbance
Blank	-	-	0.137
Blank	+	-	0.148
1	-	-	0.201
2	+	-	0.224
3	-	+	0.172
4	+	+	0.336
5	-	-	0.174
6	+	-	0.292
7	-	+	0.157
8	+	+	0.390
9	-	-	0.167
10	+	-	0.265

Subsequent trials gave even higher average concentrations and therefore an ice-bath was used during all sampling.

Figure 5.13 illustrates a calibration curve for sulphur dioxide, which was prepared because of the apparently encouraging results. The apparent dispersion of sulphur dioxide in the soil air of the dumps at Rodalquilar is given in Fig. 5.14. Flow-rates and volumes are presented in Table 5.5.

5.3.2 San Josè

Following the apparently successful modification to



ml	µg SO_2
0	0
1	0,156
2	0,312
3	0,468
4	0,624
5	0,781
6	0,937
7	1,093
8	1,249
9	1,405
10	1,562

Fig. 5.13 Calibration curve for SO_2

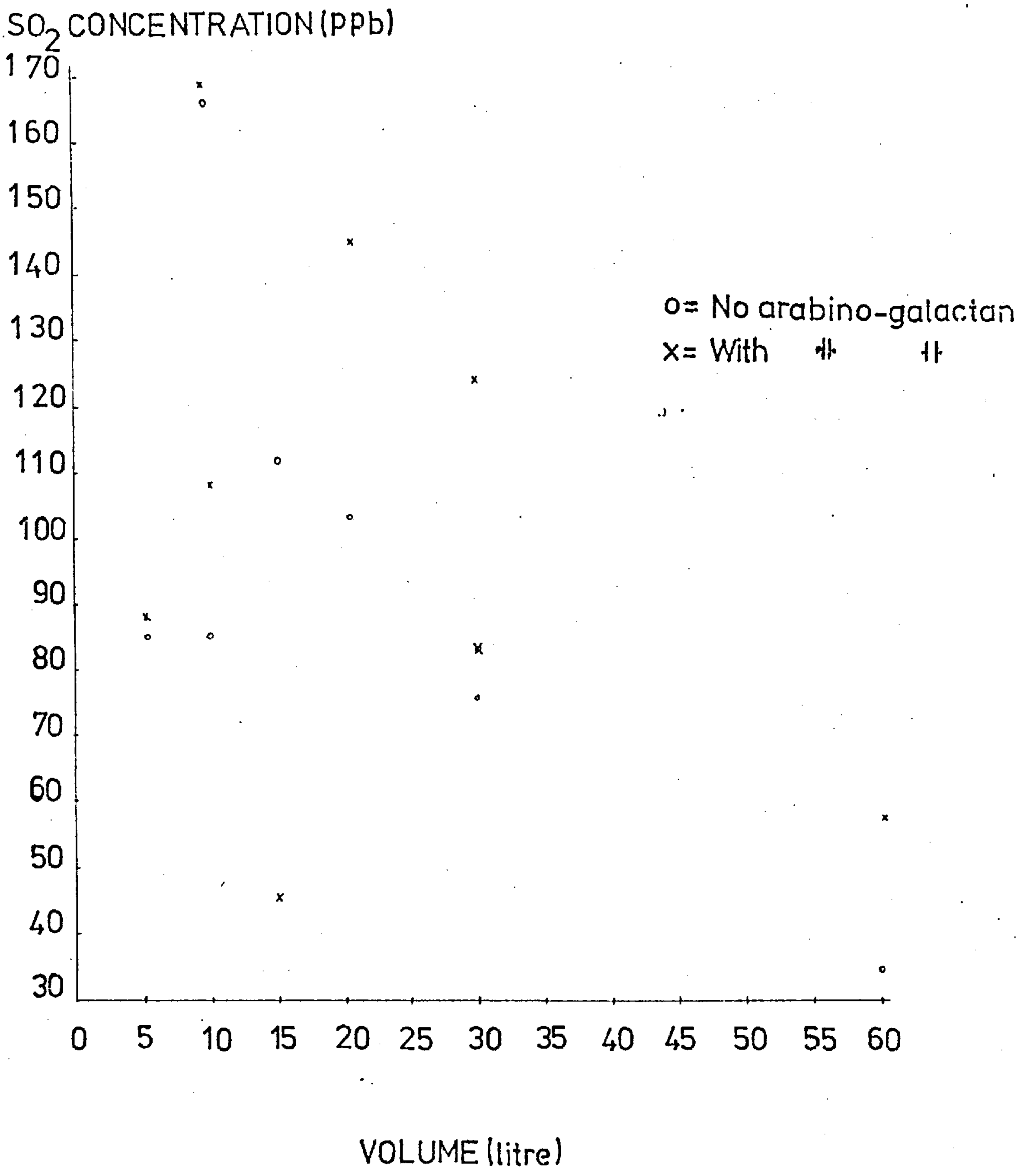


Fig. 5,14 Apparent dispersion of SO_2 in soil air of dumps at Rodalquilar

Table 5.5 Apparent SO_2 concentrations of soil air of Rodalquilar dumps

Sample	Flow-rate (ℓ/min)	Volume (ℓ)	Arabino-galactan	Concentration (ppb)
Blank			-	0
Blank			+	0
1	0.5	15	-	112.1
2	"	"	+	45.5
3	1.0	30	-	82.7
4	"	"	+	123.9
5	0.5	10	-	165.9
6	"	"	+	169.8
7	1.0	20	-	103.2
8	"	"	+	144.8
9	0.5	5	-	85.4
10	"	"	+	88.0
11	1.0	10	-	85.4
12	"	"	+	107.8
13	0.5	30	-	76.3
14	"	"	+	83.3
15	1.0	60	-	34.6
16	"	"	+	57.9
Deionized water			-	0

the technique at Rodalquilar, the next step was to attempt the detection of sulphur dioxide over concealed sulphide mineralization. The most suitable deposit in the area was selected. This was considered to be the San José sulphide-bearing vein which is described below.

The fieldarea is situated close to the village of San Josè, about 15 km south of Rodalquilar. The vegetation and climate is similar to the Rodalquilar region. A few bright-yellow dumps, containing sulphides such as galena, sphalerite, pyrite and oxidized copper minerals, produce the distinctive odour of sulphides undergoing oxidation.

Close to the village of San Josè, a 1m wide mineralized vein containing galena, sphalerite and minor chalcopyrite is exposed in volcanic rocks on both sides of a small valley (Fig. 5.15) overlain by a few metres of alluvial and colluvial sediments in the centre. Pyrite and some copper minerals occur in the wall rock and in the dumps together with galena and sphalerite in the latter as mentioned above.

5.3.2.1 Fieldwork

Tests were initially carried out on a few sulphide-bearing dumps close to the vein. The modified method for sulphur dioxide gave positive values, while hydrogen sulphide could not be detected. The sampling was thereafter transferred to the alluvium covering the mineralization, where a traverse was laid out across the vein (Fig. 5.15). The distance between the sites varied from 5m to 10m. The hard surface of the soil and the abundance of pebbles in the ground made it impossible to reach acceptable depths with either the gas auger or the hammer-probe. Depths in the range 20 - 35 cm were the maximum obtainable. A sampling-rate of 0.5 ℓ/min over a period of 20 minutes was used. About six full days were

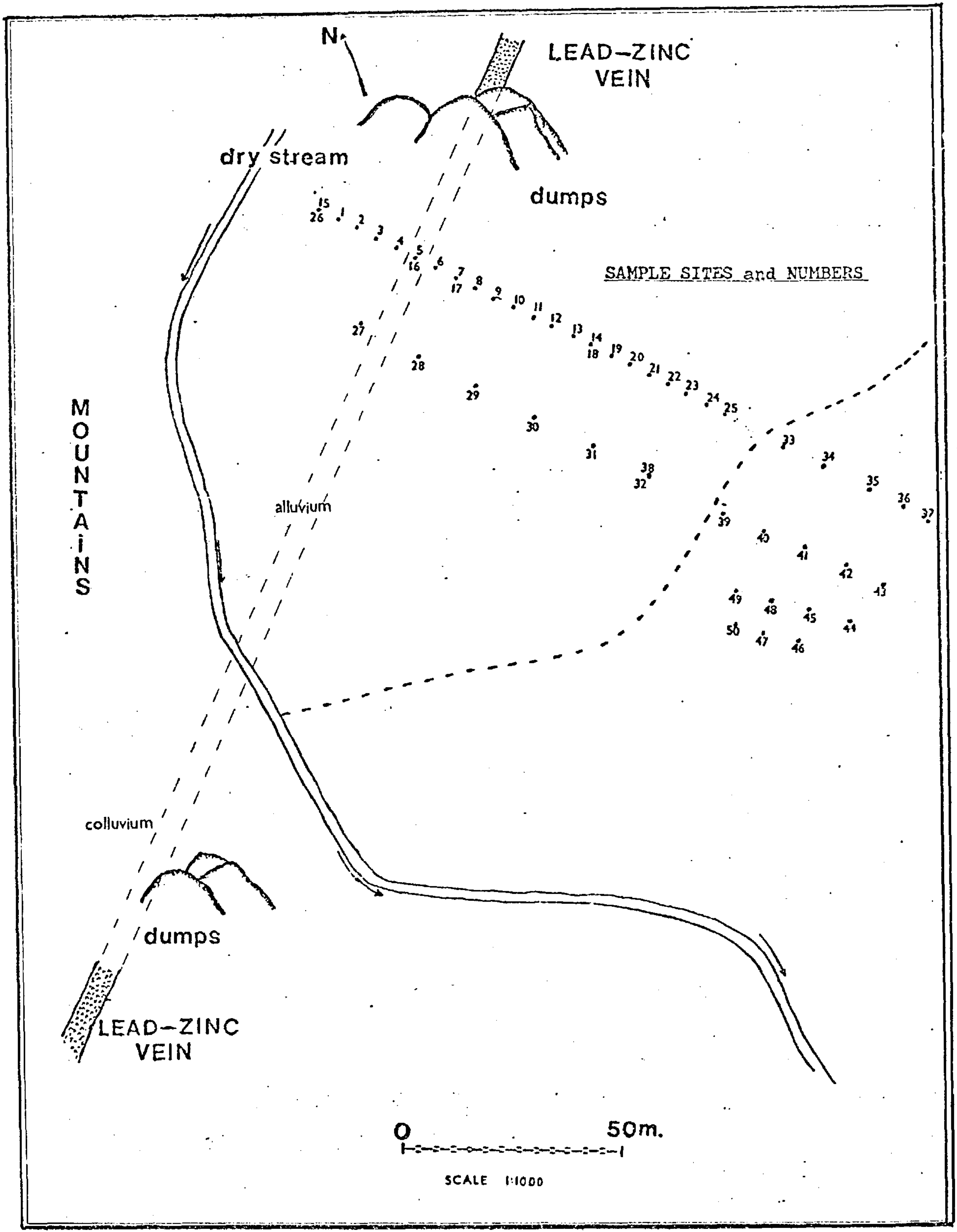


Fig. 5.15 San Josè fieldarea

spent working on the traverse.

Hydrogen sulphide was not detected in the soil atmosphere or in the free atmosphere in the area. The apparent concentrations of sulphur dioxide in the soil air are given in Table 5.6 and Fig. 5.16 - 5.17.

The extremely high apparent concentrations of sulphur dioxide in the soil air 80 - 90m east of the concealed mineralization were suspect and could not be explained until a careful examination of the sampling device revealed that the plastic filter-holder had been damaged. The high temperature, the intensive sun radiation and the numerous stones on the ground had all contributed to this damage to such a degree that numerous cracks and fractures had been formed. A strong odour was evolved. The gas, produced from the filter-holder, is thought to be an aldehyde which would react with the pararosaniline.

5.3.3 Additional fieldwork

After removing the filter-holder, the sampling of soil air continued on sulphide-rich dumps in the San Josè as well as in the Rodalquilar fieldareas in attempts to detect sulphur dioxide. Results were negative.

Finally, a series of large plastic-lined cardboard boxes (60 x 35 x 5 cm) were laid out on the dumps and left for 24 hours after sealing the edges with soil and stones to ensure that no dilution of sulphur dioxide, evolved from the surface of the ground and the soil atmosphere, took place. The atmosphere within the boxes was sampled via a small hole

Table 5.6 Concentrations of apparent SO_2 in soil air at San José, S-E Spain (flow-rate: 0.5 ℓ/min; volume: 10 ℓ)

Sample	Time of day	Concentrations
1	16.30 - 16.50	43.2
2	16.01 - 16.21	28.6
3	15.32 - 15.52	28.3
4	15.05 - 15.25	34.3
5	12.07 - 12.27	55.2
6	12.37 - 12.57	50.7
7	13.10 - 13.30	65.6
8	13.45 - 14.05	76.0
9	14.23 - 14.43	75.2
10	11.20 - 11.40	32.2
11	12.35 - 12.55	76.0
12	13.00 - 13.20	71.6
13	13.28 - 13.48	79.0
14	13.55 - 14.15	122.3
15	14.25 - 14.45	42.3
16	14.50 - 15.10	55.2
17	15.15 - 15.35	76.0
18	10.15 - 10.35	24.2
19	10.40 - 11.00	24.5
20	11.05 - 11.25	27.7
21	11.30 - 11.50	23.9
22	12.00 - 12.20	35.8
23	12.20 - 12.40	28.0
24	13.05 - 13.25	61.1
25	13.30 - 13.50	52.2
26	14.10 - 14.30	59.6
27	14.35 - 14.55	37.3
28	15.00 - 15.20	64.1
29	15.25 - 15.45	51.9
30	15.55 - 16.15	85.0
31	16.20 - 16.40	40.6
32	16.40 - 17.00	141.7
33	9.35 - 9.55	55.2
34	10.00 - 10.20	17.9
35	10.30 - 10.50	26.8
36	10.55 - 11.15	55.2
37	11.20 - 11.40	79.0
38	13.40 - 14.00	305.7
39	13.16 - 13.36	286.3
40	12.53 - 13.13	219.2
41	12.30 - 12.50	0
42	12.05 - 12.25	86.5

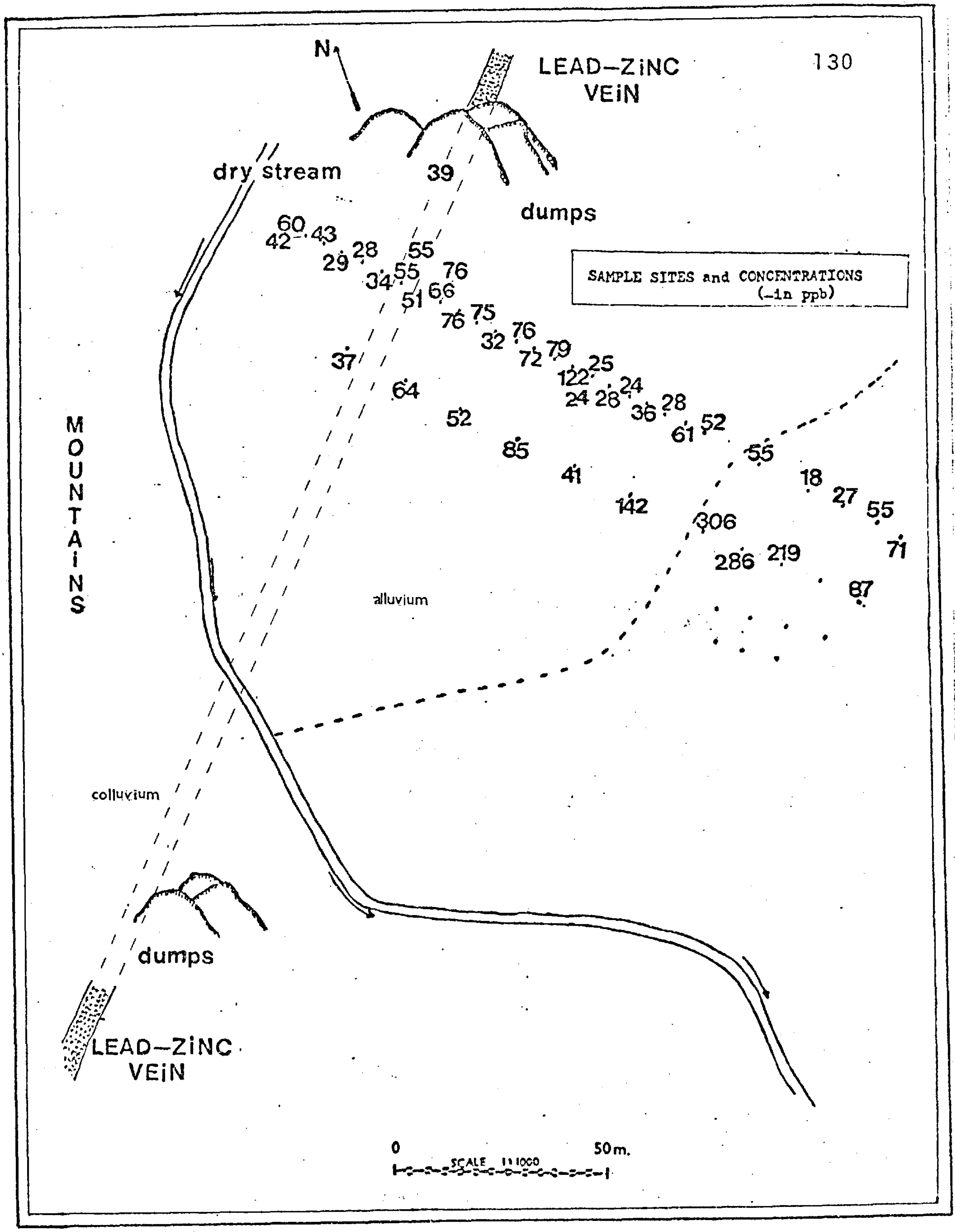


Fig. 5.16 Apparent concentrations of sulphur dioxide in the soil air, San José, S.E. Spain

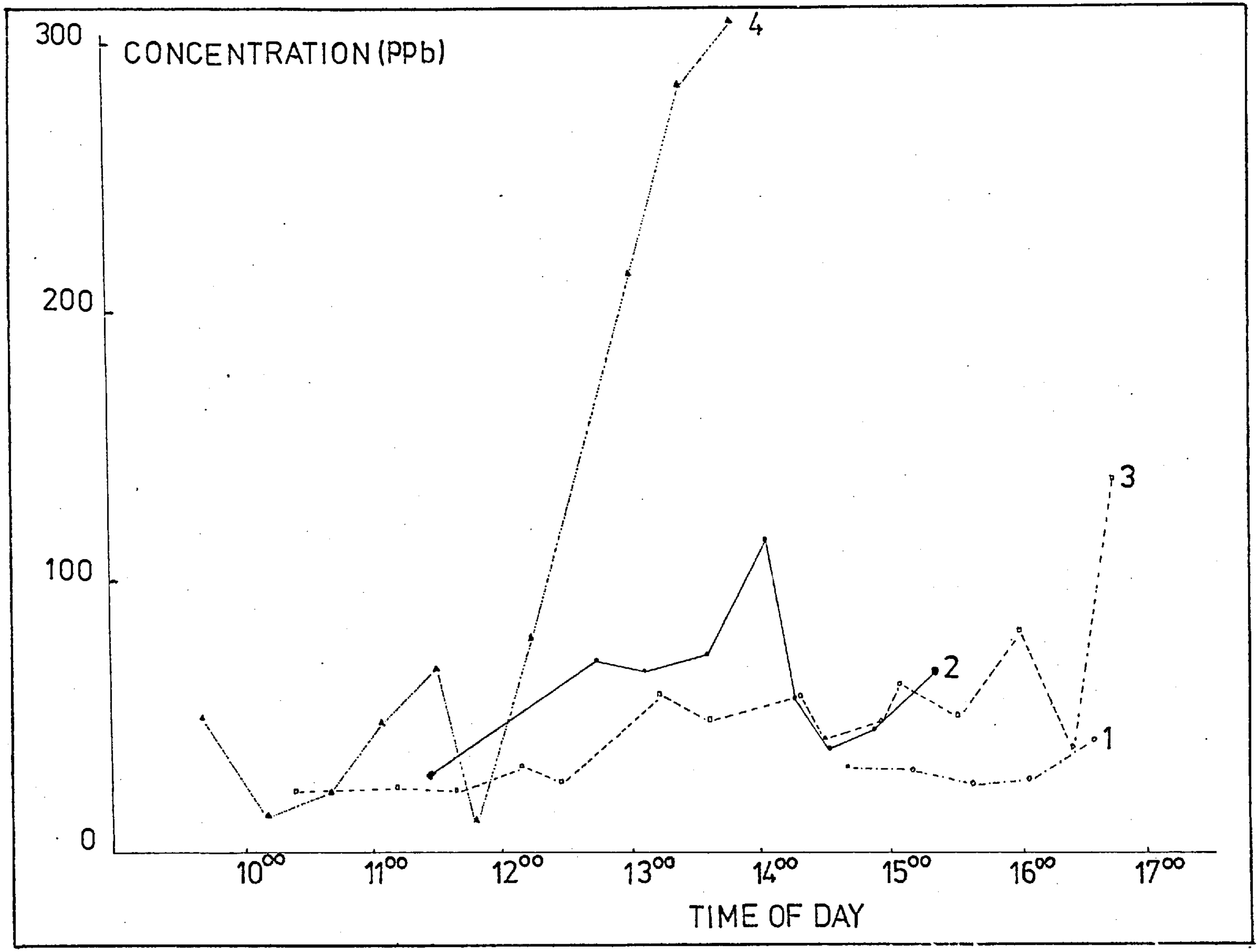


Fig. 5.17 Variation of apparent SO_2 concentration with time during four days

in the top. The results from this procedure are presented in Table 5.7 and Fig. 5.18.

Table 5.7 Concentrations of sulphur dioxide in the lower atmosphere over a Rodalquilar dump

Sample	Flow-rate (ℓ/min)	Volume (ℓ)	Concentration (ppb)
1	1.0	7	71.1
2	0.5	3.5	65.5
3	0.5	3.5	63.9
4	1.0	7	40.5
5	0.5	10	40.3
6	1.0	20	22.1
7	1.0	150	-

Sampling of the free atmosphere, without boxes, over a Rodalquilar dump gave negative results. Despite a strong odour of sulphur in an adit, sulphur dioxide was not detected.

Ambient air concentrations of sulphur dioxide in the range 10 - 20 ppb were measured using the Gastec gas detector in the adit in the Rodalquilar area. This analytical device consists of two essential parts, a piston-type volumetric pump (max. 100 ml air sample in each stroke) and a sampling tube, specific for sulphur dioxide.

The sampling tube contains sodium hydroxide which is neutralized by sulphur dioxide and the colour of the pH indicator (phenol red) is changed:

$$SO_2 + 2NaOH \rightarrow Na_2SO_3 + H_2O$$

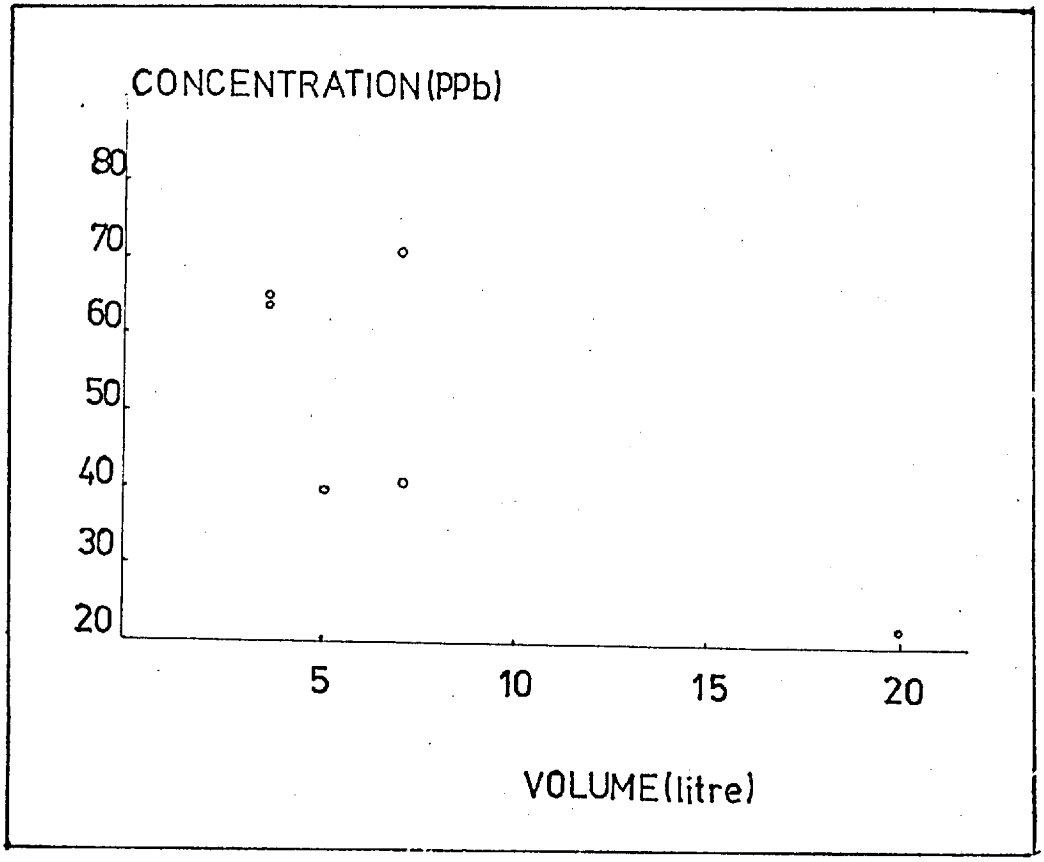


Fig. 5.18 Concentration versus sample volume for sulphur dioxide in the lower atmosphere over a Rodalquilar dump

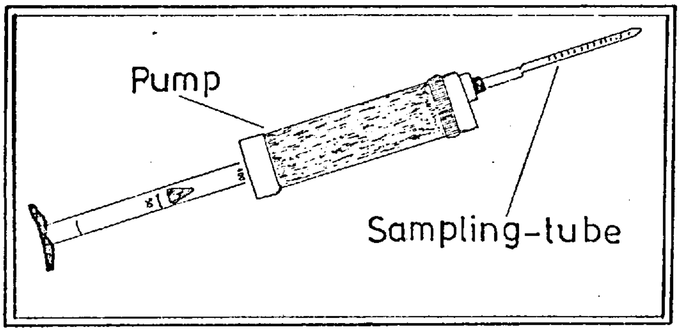


Fig. 5.19 Gastec gas detector

The length of the discoloration is a measure of the concentration, which is read directly on the graded tube. The claimed detection limit is 0.2 ppm for a 0.4 ℓ sample.

Hydrogen sulphide was not detected using the Gastec gas detector. The sampling tube for hydrogen sulphide consists of lead acetate that reacts with hydrogen sulphide forming pale brown lead sulphide. The reaction principle is:

$$H_2S + Pb^{2+} \rightarrow PbS + 2H^+$$

The claimed detection limit is 0.1 ppm for a 1 ℓ sample.

Some soil samples from the dumps in the Rodalquilar area were brought to London, where further experiments were carried out. The odour of oxidizing sulphides was only noticeable over the samples after they had been heated; at room temperature they had no odour.

A sample was placed in a desiccator and kept at room temperature for one week. The air in the desiccator was then drawn into a scrubber containing the tetrachloromercurate absorbing solution and arabino-galactan with the aid of the usual sampling device and a vacuum pump. Three tests were carried out giving sulphur dioxide concentrations in the range 17 - 26 ppb; similar to those found in the adit air in the Rodalquilar area using the Gastec gas detector.

5.4 Conclusions

The discouraging results from the investigation of sulphur dioxide and hydrogen sulphide in relation to sulphide mineralization may be explained in many ways.

Both gases are absorbed by wet and dry soils according to Smith et al (1973) and Bremner and Banwart (1976). The low concentration of sulphur dioxide in proximity to the sulphide-rich dumps in the fieldareas suggests that only a minor amount is emitted to the free atmosphere. Another natural explanation may be that traces of metals such as Fe and Mn may have entered the absorbing solution for sulphur dioxide which subsequently act as catalysts in the oxidation of sulphur dioxide. The trials with the permeation tubes after the fieldwork indicate that sulphur dioxide is lost in the sampling system to an amount of 20 - 60 percent depending on flow-rate and sample volume.

Negative results using sulphur dioxide as an indicator of oxidizing sulphides were also reported by other members of the team. M. Hale and J. Lovell were unsuccessful in detecting sulphur dioxide in a 240 ℓ sample, collected over sulphides under rainy conditions and analysed using the original West-Gaeke method (Internal Report, 1975).

The most likely conclusion is considered to be that the gaseous compounds evolved from oxidizing sulphide deposits are not sulphur dioxide and hydrogen sulphide. The physiological threshold for the odour of these two gases is 10 - 25 ppb for hydrogen sulphide and 0.5 - 2 ppm for sulphur dioxide. Both are well above the detection limit of the methods used even with unefficient sampling. The present investigation, carried out in two areas with different climatological conditions, suggests that these two gases are not suitable to use as pathfinders for weathering sulphides. The fieldtests gave no indication of any relationship between the two gases and sulphide-bearing deposits.

As no hydrogen sulphide and only minor amounts of sulphur dioxide in a few samples were detected, it was concluded that the odour from sulphide-bearing dumps and mines was probably due to other sulphur gases such as organic gaseous compounds.

CHAPTER 6

DEVELOPMENT OF GAS CHROMATOGRAPHIC TECHNIQUES FOR EXPLORATION PURPOSES

6.1 Introduction

Since the investigations outlined in previous chapters showed that gases other than sulphur dioxide and hydrogen sulphide are emitted from oxidizing sulphides, it was decided to investigate the possibility of other gaseous sulphur compounds. The most promising sensitive technique, as suggested in the literature, for the simultaneous analysis of sulphur volatiles was gas chromatography using a flame photometric detector. The correctness of this decision was confirmed by the results obtained by Margaret Hinkle of the U.S. Geological Survey who reported that she had used a gas chromatograph together with a flame photometric detector (Melpar detector) in the analysis of sulphur gases collected by molecular sieves over oxidizing sulphides (written communication, 1975). Her investigation confirmed that small amounts, if any at all, of sulphur dioxide were evolved but large amounts of carbonyl

Table 5.8 Summary of results obtained in the fieldareas in all of which presumed sulphur gas was detectable

Fieldarea	Background SO_2 (ppb)	SO_2 over mineralization (ppb)	Background H_2S (ppb)	H_2S over mineralization (ppb)
Trefriw, Wales	n.d.	n.d. - 15.3[a]	n.d.	n.d.
Parys Mountain, Wales	n.d.	n.d.	n.d.	n.d.
Rodalquilar, Spain	n.d.	n.d. - 71.1[b]	n.d.	n.d.
San Jose, Spain	n.d.	n.d.	n.d.	n.d.
Threshold for physiological detection of odour		0.5 - 2 ppm		10 - 25 ppb
Detection limit of analytical method	3 ppb		3.5 ppb	

n.d. = not detected

a = 12 samples out of 16 samples gave n.d.

b = 128 samples out of 134 samples gave n.d.; positive results were only obtained when using the plastic-lined cardboard boxes described in the text above. A few tests with the Gastec gas detector is not included in Table 5.8. Both soil air and atmospheric samples are included in the total number of samples.

sulphide were detected.

In the following sections, the theory of gas chromatography is outlined, followed by previous work on gas chromatographic analysis of sulphur gases (mostly in the ppm range). Experimental work aimed at detecting at least six organic and inorganic sulphur gases in the low (ppb) range was undertaken, the results of which are given below. The necessity of increasing sensitivity was dictated by the very low levels to be expected in soil gas under natural conditions.

6.2 The Technique of Gas Chromatography

Gas ghromatography is a method of separating the components of a gaseous mixture by passing the vapour through a column containing a compound for which the individual gaseous components have varying affinity. Those with a stronger affinity are retained for longer times and are thus separated on their way through the column. The vapour concentrations leaving the column are recorded by means of a suitable detector. The signal is amplified and operates a chart recorder to produce chromatograms. These consist of a number of peaks or elution curves, each of which corresponds to a component of the mixture and the position (i.e. time differential) of each of these deflections is characteristic of each different gas passing through the column. Parameters such as type, length and diameter of column, operating temperature, heating rate, type of column packing and gas flow-rates are all of importance in the separation of the gases.

The gas chromatographic system is composed of flow-controllers, sample injection method, column, column oven, detector, carrier gas, auxiliary gas supplies, amplifiers power supply and a chart recorder. In the present research, different types of columns and carrier gases have been used and are described below. The detector used in the analysis of sulphur volatiles is the flame photometric detector (FPD), which will be described below.

6.2.1 Flame photometric detector for sulphur gas analysis

The original flame photometric detector, for sulphur compounds in air was described in a patent by Draeger in 1962 and was further modified for gas chromatographic use by Brody and Chaney (Ronkainen et al, 1973).

When effluent sulphur compounds from the column are burnt in a cool hydrogen-rich, mixed air-hydrogen flame, a strong blue chemiluminescence is emitted due to the formation of the S_2 molecule following the reaction:

$$S + S \rightarrow S_2 + hv$$

(hv is the energy of a single photon, where h is Planck's constant and v is the frequency of the radiation)

Since two atoms are required, the intensity of the radiation is proportional to the square of the concentration of the sulphur compound in the flame (for compounds containing only one sulphur atom). The combustion zone is recessed in a barrel, which acts as a light shield. The tip of the flame is exposed to a photomultiplier tube through a narrow bandpass optical interference filter, which transmits only the strong band at 3940Å for sulphur by an electrometer to a potentiometric recorder. Compounds, which do not contain sulphur do not cause an emission at this wavelength in a cool hydrogen-rich flame and therefore are not detected with the flame photometric detector (Melpar detector). Ronkainen et al (1973) state that compounds such as carbon dioxide and ethanol in higher concentrations do cause a detector response, but that the specific sensitivity of the detector is much greater for sulphur than for other compounds at this wavelength.

The detector performance and sensitivity are determined by the magnitude of the drift and noise associated with the flame background emission. These are in turn strongly affected by the flame temperature and gas flow-rates. The detection limit of a gas chromatographic system is determined by factors such as background noise, column material and instrumental parameters.

6.2.2 The chromatographic column

The efficiency is the separating power of a column (Fig. 6.1) and is related to the number of theoretical plates or equal sections which a column may be considered to consist of. If n is the number of theoretical plates in a column, we get:

$$n = \left(\frac{b}{a}\right)^2$$

where b is the retention distance of a component and a is the half-width of a peak between its points of intersection with the tangents of inflection, assuming the peak is of Gaussian form. The width of the peak at the base, i.e. the distance between the points of intersections of these tangents and the base-line of the chromatogram is 4a = w. The number of theoretical plates can now be rewritten as:

$$n = 16\left(\frac{t}{w}\right)^2$$

where t is the retention time of the component and where w is the width in time-units between the tangential intersections with the baseline. The narrower the peak, the better is the efficiency. M on Fig. 6.1 is the maximal point on the peak related to component A. To reach this value, a definite volume of carrier gas passed through the column (retention volume). Retention volume/carrier gas flow-rate is the retention time, which is affected by column temperature, flow-rate of carrier gas, length of column and column packing and is the distance OP(t) on the model chromatogram (Fig. 6.1). In the experiments carried out, all retention times were measured relative to the injection point. The separation factor (peak resolution) is defined as:

$$\frac{2 \text{ x distance from one maximal peak height to the other}}{\text{sum of the base of each peak}}$$

$$= \frac{2PD}{RS + YZ}$$

The separation factor is considered to be satisfactory when it exceeds unity. Adsorption on the column packing material and column walls results in asymmetric peaks (tailing)

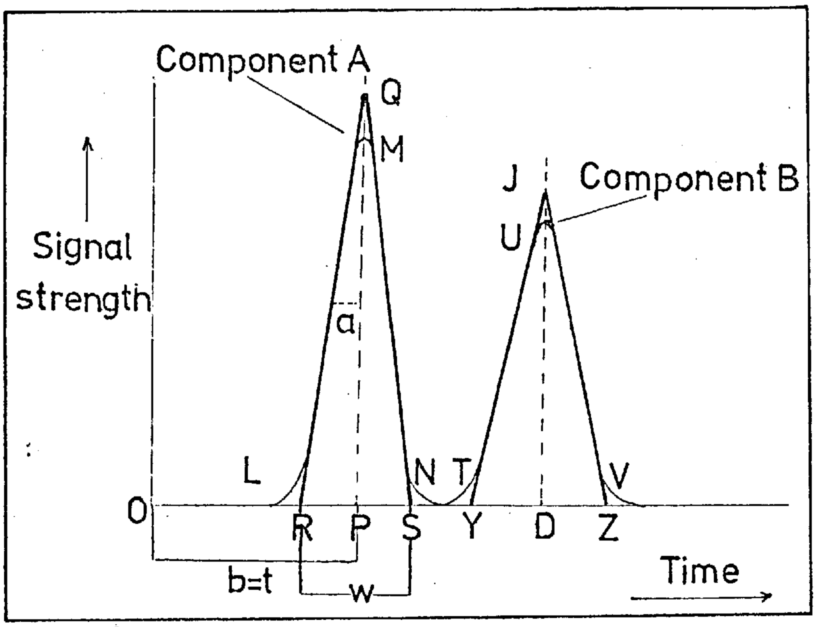


Fig. 6.1 Model chromatogram for calculation of column efficiency, retention time, etc.

and poor separation between components (Fig. 6.2). The concentration of a component is related to the area of the peak. For component A on Fig. 6.1, the peak area is 0.5 x LN x PM, which can be measured by an integrator directly connected to the chart recorder.

6.3 Previous Work on Sulphur Gas Chromatography

Much work has been undertaken analysing sulphur gases such as hydrogen sulphide, sulphur dioxide and methyl mercaptan, present in ppm levels using the gas chromatographic system (Kremer and Spicer, 1973; Bollman and Mortimore, 1972; Obermiller and Charlier, 1969; Zlatkis et al, 1970; Thornsberry, 1971). Serious problems have been reported in the analysis and separation of sulphur gases in the lower ppb

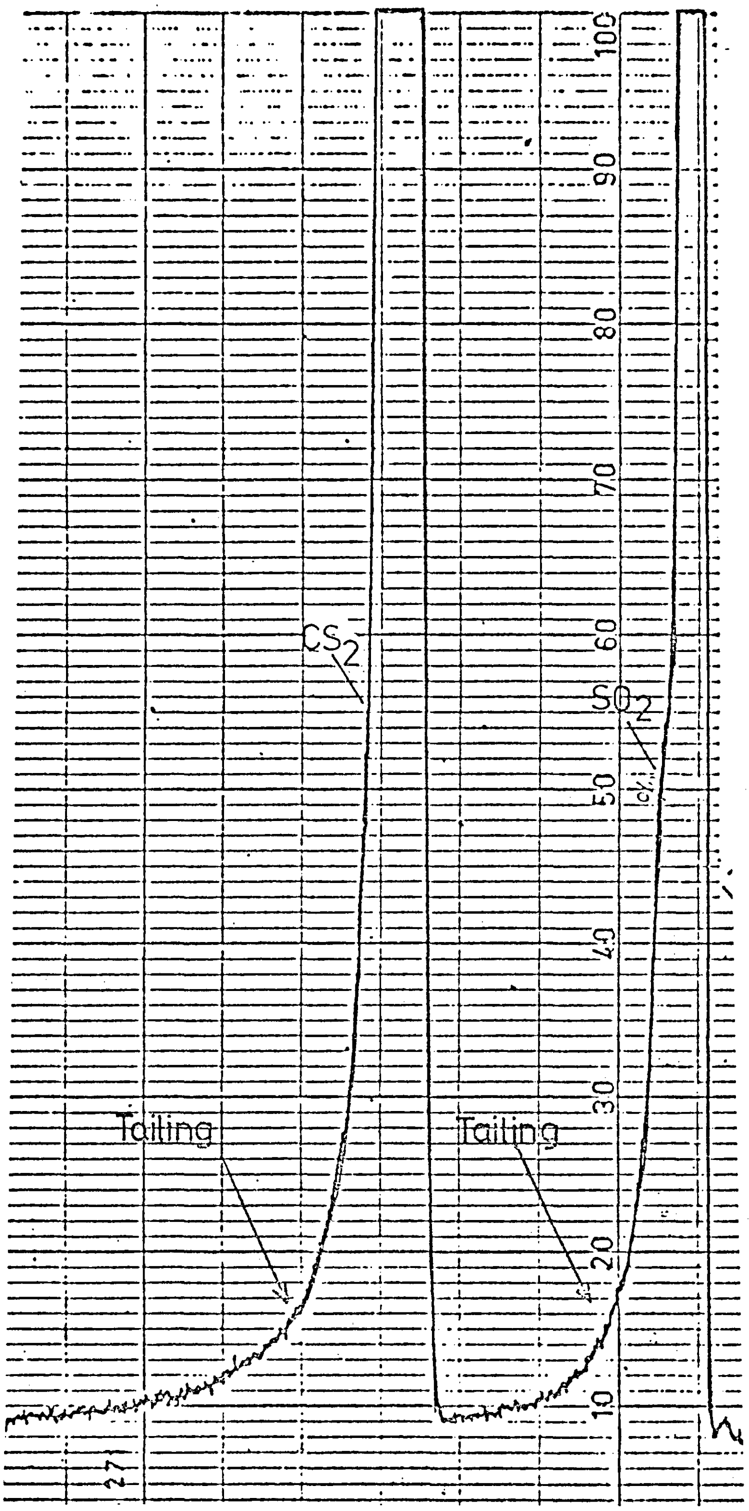


Fig. 6.2 Chromatogram showing tailing

concentration range with which we are concerned. Irreversible adsorption problems on column walls and packing and lack of instrumental sensitivity are the main negative factors (Stevens et al, 1971). Many unsuccessful attempts have been made to separate and analyse sulphur gases below the ppm level (Bruner et al, 1975; Stevens et al, 1969, 1971).

The selection of an appropriate column to obtain a specific performance is essential in gas chromatographic analysis, particularly when strongly reactive and polar compounds have to be determined qualitatively at very low concentrations. Glass, Teflon, stainless steel and aluminium columns, packed with a wide variety of compounds have been evaluated by numerous workers (Bruner et al, 1972, 1975; Stevens et al, 1969, 1971; Ronkainen et al, 1973; Souza et al, 1975). Most of them mention problems in measuring sulphur volatiles below the ppm level. Metals have been reported to be strongly adsorptive to sulphur compounds, causing serious losses when the gases are present below the 10 ppm level (Kremer and Spicer, 1973; Ronkainen et al, 1973; Bremner et al, 1975). Teflon (PTFE) has become popular as column container due to its inactivity and non-adsorptive properties to sulphur (Stevens et al, 1971; Rasmussen, 1974; Souza et al, 1975).

One of the more attractive techniques for the detection of sulphur volatiles in the lower ppm concentration range is a procedure developed by Souza et al (1975) who succeeded in separating six organic and inorganic sulphur volatiles in 7 minutes transit time, through the column, including the separation of hydrogen sulphide from carbonyl sulphide which had caused problems (Kremer and Spicer, 1973). Much of the present work has been based on the procedure suggested by Souza et al (1975). A detailed description of the technique is given below together with two other procedures, used in the analysis of sulphur gases in the ppm and ppb levels.

The chromatogram in Fig. 6.3 shows the separation of four volatile sulphur compounds on a column developed by Stevens et al (1971).

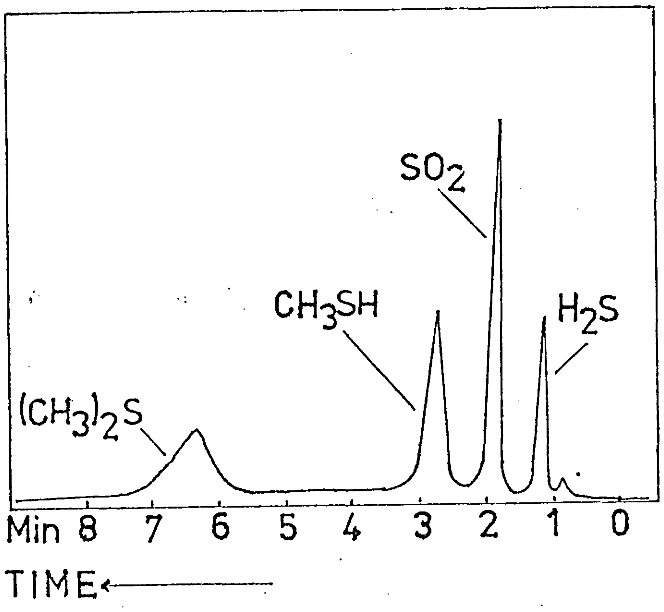


Fig. 6.3 Chromatogram showing separation of sulphur gases in concentrations below 1 ppm (after Stevens et al, 1971)

The following materials and conditions were used. Column: 36 ft x ⅛-inch inner diameter Teflon packed with polyphenyl ether/phosphoric acid on 40/60 mesh Haloport F (powdered Teflon); Conditioning of column at 140°C for 6 hours; Temperatures: Oven 50°C; Detector 105°C; Exhaust 110°C; Flows: Nitrogen carrier gas 100 ml/min; Oxygen 15 ml/min; Hydrogen 75 ml/min. The disadvantages are: poor performance for carbonyl sulphide, carbon disulphide and dimethyl disulphide.

Fig. 6.4 illustrates separation of hydrogen sulphide, sulphur dioxide, methyl mercaptan and dimethyl sulphide on a column prepared by Bruner et al (1972).

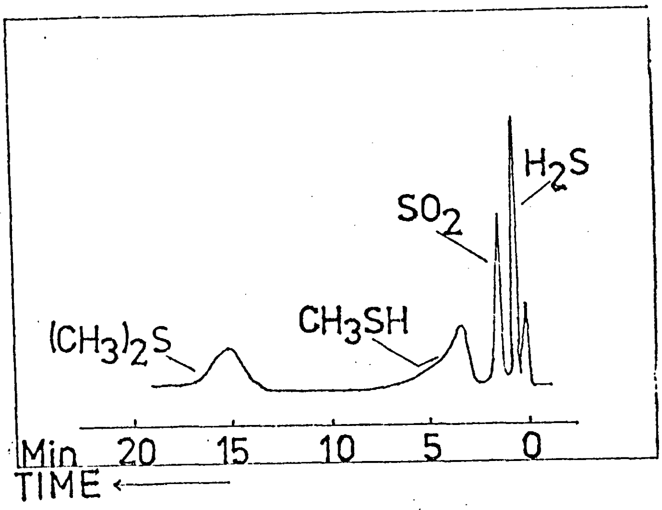


Fig. 6.4 Chromatogram showing separation of sulphur gases in concentrations down to 30 ppb (Bruner et al, 1972)

The following materials and conditions were used. Column: 1.25m x 3mm inner diameter Teflon packed with acid-treated graphitized carbon black; Temperatures: oven 40°C; detector 115°C; Flows: nitrogen carrier gas 100 ml/min; oxygen 10 ml/min; air 30 ml/min; hydrogen 150 ml/min. The disadvantages are poor separation of sulphur dioxide and hydrogen sulphide above 80°C; long elution time and unsatisfactory performance of carbon disulphide, carbonyl sulphide and dimethyl disulphide, and tailing problems for the peak for methyl mercaptan.

Fig. 6.5 shows a column developed by Souza et al (1975) in which hydrogen sulphide and carbonyl sulphide are separated from each other. Dimethyl disulphide is eluted in less than 7 minutes together with another five sulphur compounds. There is however no separation of carbon disulphide and dimethyl sulphide.

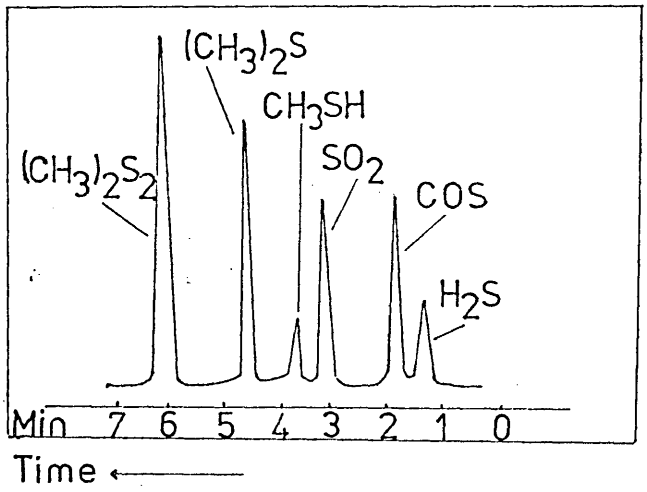


Fig. 6.5 Separation of sulphur gases in the low ppm concentration range (Souza et al, 1975)

The following materials and conditions were used. Column: 40 cm x 3mm diameter acetone-washed Teflon packed with 60 - 80 mesh acetone-washed porapak QS; conditioning of column overnight at 240°C. Temperatures: oven 30°C - 210°C by 40°C/min increment; post-injection delay of 1 min; detector temperature 115°C. Flows: helium carrier gas 31 ml/min; air 50 ml/min; hydrogen 155 ml/min; oxygen 15 ml/min. The disadvantages are no separation of carbon disulphide and dimethyl sulphide.

Prior to the decision to acquire a gas chromatograph, initial preliminary tests were carried out by other members of the team (Professor J.S. Webb and J. Lovell) who analysed headspace gas samples over sulphide and soil in the Techmation laboratories. The samples were taken and presented to the gas chromatograph with a 1 ml Hamilton gastight hypodermic syringe. The results are presented in the following chromatograms. Fig. 6.6 shows two peaks derived from ambient air. The first is a pressure peak and the effect of the oxygen in the sample on the flame and the second peak represents ambient sulphur dioxide. Fig. 6.7 shows two peaks, which differ very little from the previous sample, from background soil from Rodalquilar, S.E. Spain. Fig. 6.8 shows a chromatogram obtained from oxidizing sulphides from dumps in the Rodalquilar area. Carbonyl sulphide or hydrogen sulphide (the retention times of these two compounds are almost the same due to the column and temperature used), sulphur dioxide and an unknown gas, present as the major peak, were detected. Fig. 6.9 illustrates a chromatogram obtained from crushed galena from the dumps at San Josè, S.E. Spain. Hydrogen sulphide or carbonyl sulphide, sulphur dioxide and the unknown gas are present. Fig. 6.10 shows that the unknown gas is represented as the major peak of this sulphide sample from Parys Mountain.

In these preliminary tests, carried out under specific conditions, two unidentified gases were found to be the

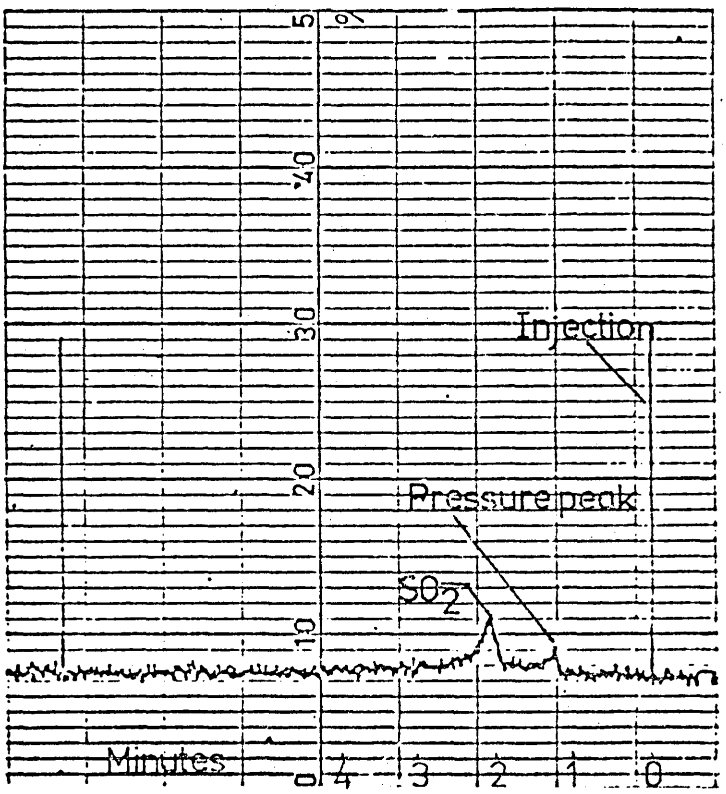


Fig. 6.6 Gas chromatographic analysis of ambient air

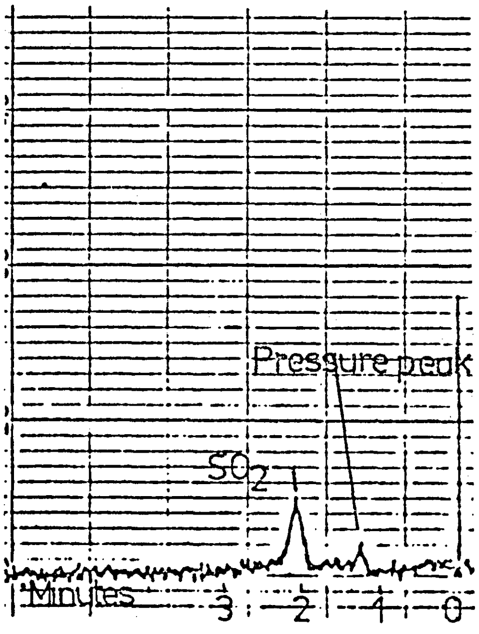


Fig. 6.7 Gas chromatographic analysis of the headspace gas of a Rodalquilar background soil sample

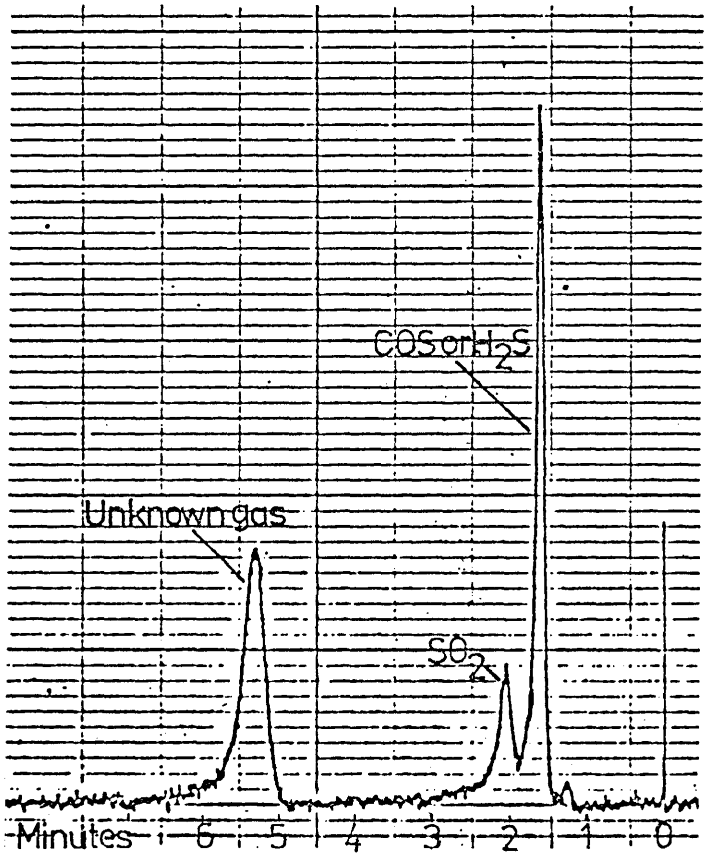


Fig. 6.8 Gas chromatographic analysis of the headspace gas over oxidizing sulphides from a Rodalquilar dump

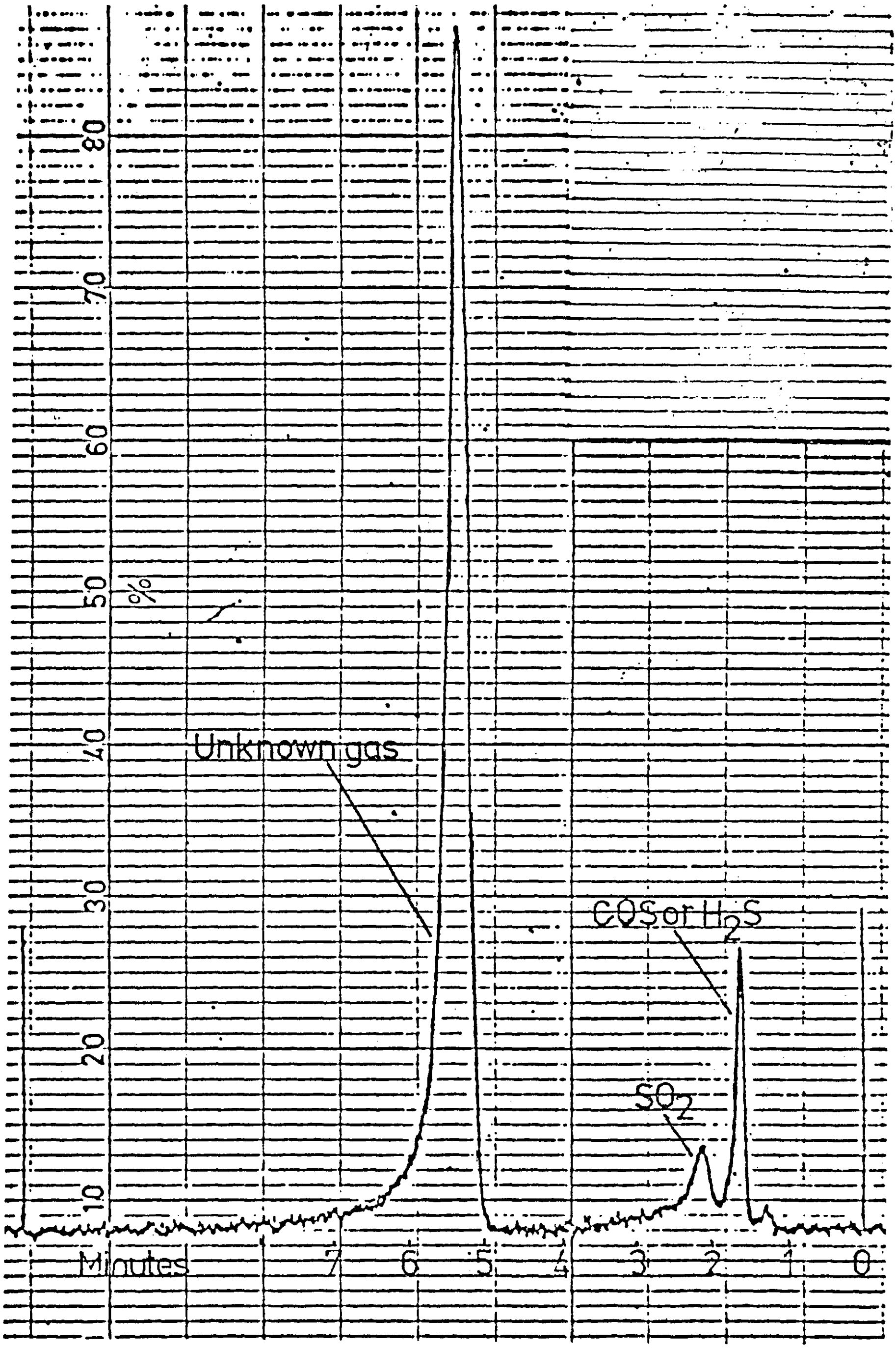


Fig. 6.9 Headspace gas of crushed galena from San Josè

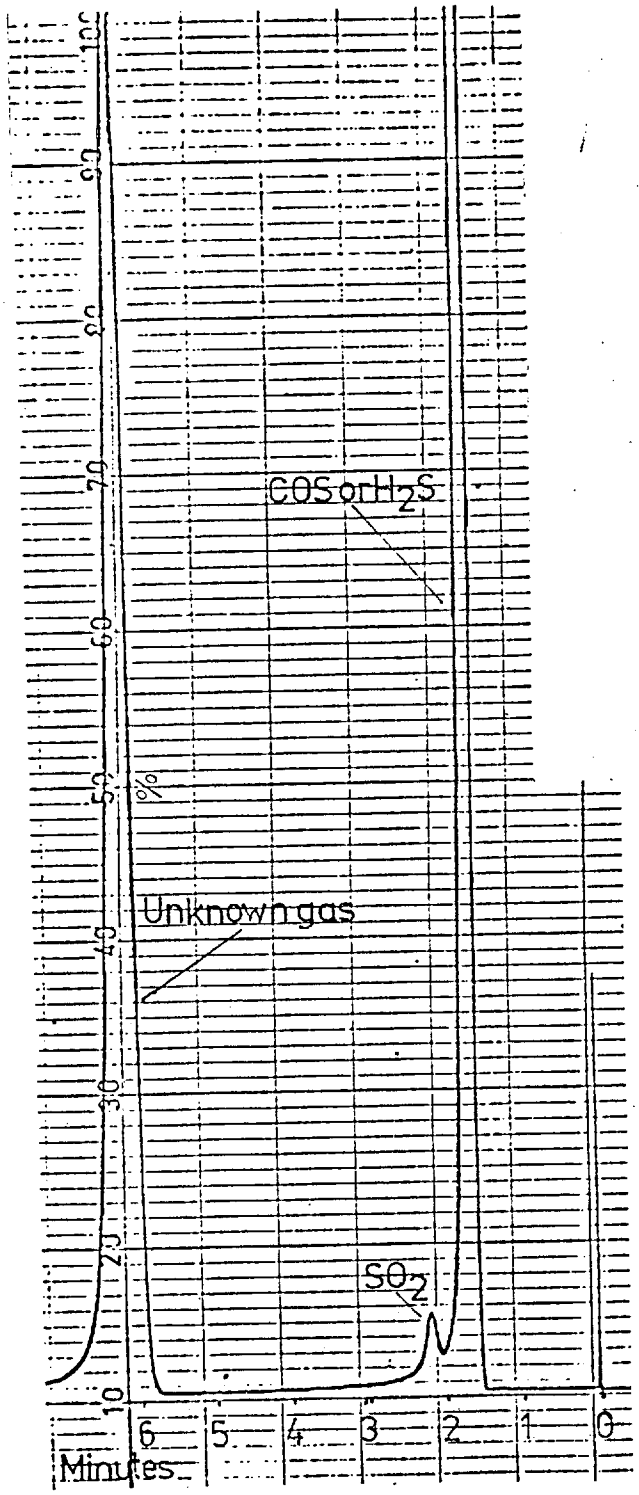


Fig. 6,10 Gas chromatographic analysis of the headspace gas over sulphides from Parys Mountain major components in the headspace gas over sulphides contained in closed glassbottles. Sulphur dioxide was only found to be present at ambient air levels confirming the conclusions drawn from previous experimental fieldwork and M. Hinkle's observations.

6.4 Experimental Work

6.4.1 Introduction

The scope of the work on gas chromatography has included the use of different gas chromatographic instruments, column materials and packings and operational conditions. The aim of the work was to develop a procedure in which as many relevant sulphur gases as possible could be qualitatively determined simultaneously.

A technique has been developed in which six sulphur gases can be separated and a desorption system has been designed in which adsorption cartridges, used for collection of samples in the field, are heated prior to analysis. The lack of time has not allowed any quantitative calibration of either of the instruments used.

A description of the two instruments is given below, followed by a presentation of the development of a gas chromatographic analytical procedure, in which six organic and inorganic sulphur volatiles were separated as well as the subsequent fieldwork (Chapter 7).

6.4.2 Description of the gas chromatographs used in the analysis of sulphur volatiles

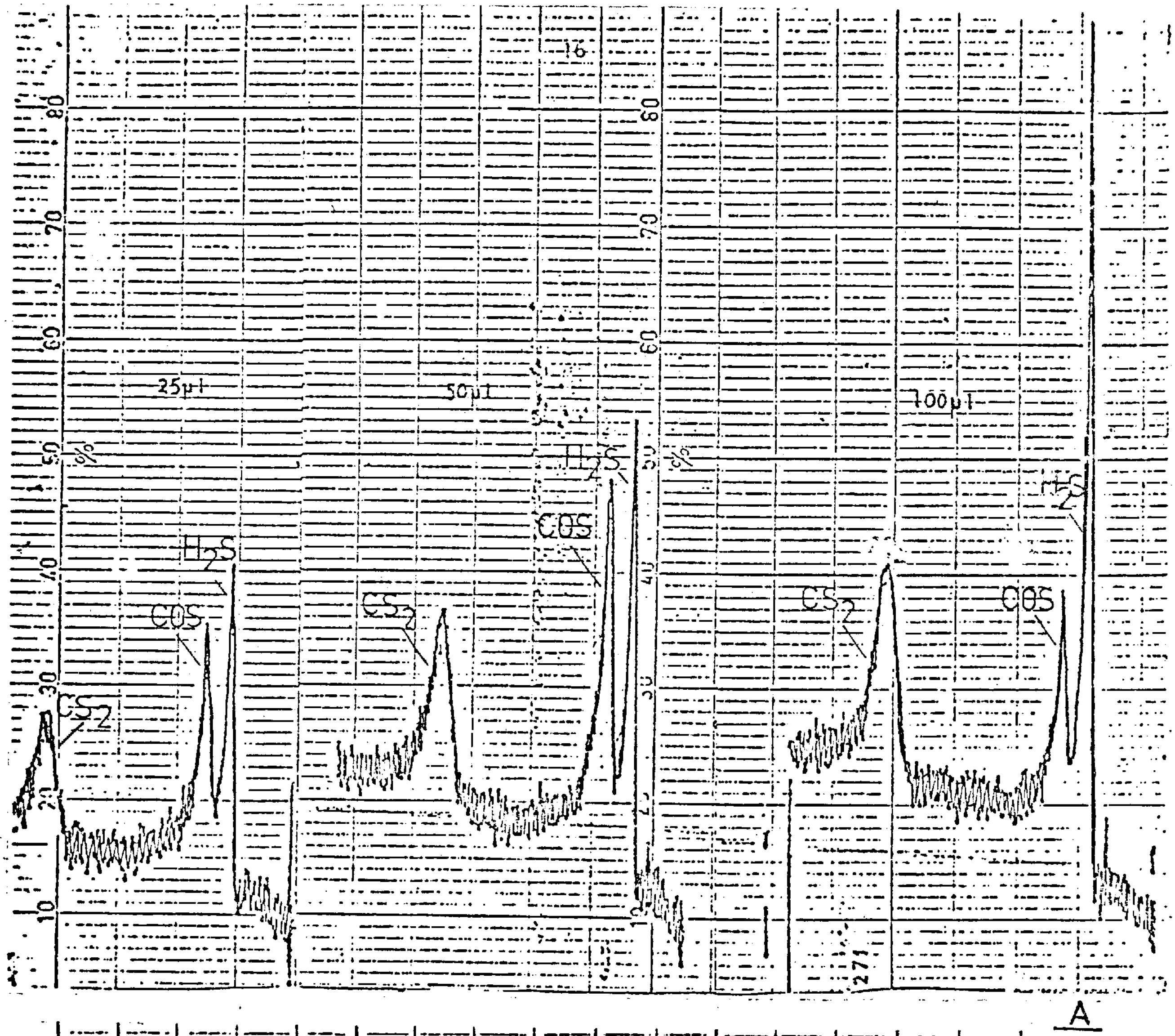
Based on the encouraging results obtained during the preliminary experiments using a Tracor gas chromatograph at Techmation Ltd., two instruments were considered: the Perkin-Elmer F17 and the Tracor 560.

The Perkin-Elmer F17 gas chromatograph was originally selected because of lower cost and claimed performance. Unsatisfactory sensitivity, erratic baseline and the tendency for the hydrogen-rich flame to extinguish each time a sample was injected contributed to the replacement of this instrument by the Tracor 560. Specifications for both instruments are given in Table 6.1. Facilities for using detectors such as the flame ionization detector (FID) and the electron capture detector (ECD) are provided for the Perkin-Elmer F17 instrument, while the Tracor 560 gas chromatograph is provided with a facility for operation of the Meloy FPD and FID mode.

Both instruments were operated simultaneously and identical samples were presented to both devices. The Tracor 560 gas chromatograph was found to be more suitable for our needs due to its higher sensitivity, better digitized electronic controls with more operational facilities and a better chromatographic performance for sulphur gases in the lower concentration ranges required. The chromatograms shown in Fig. 6.11 illustrate the performance of the two instruments. The baseline on the Tracor 560 is more constant and the peaks of the gaseous compounds are more evident than on the chromatogram obtained by using the Perkin-Elmer F17.

Table 6.1 Specifications for Perkin-Elmer F17 and Tracor 560 gas chromatographs

	Perkin-Elmer F17	Tracor 560
Column oven		
Temperature range	50°C - 450°C	Ambient - 400°C
Cool down and restabilization time	250°C to 100°C in 8 minutes	250°C to 50°C in 8 minutes
Temperature programmer		
Initial isothermal period	0,2,4,6,8,10,12,14,16,32 minutes	1-999 min. in 1 min. increments
Final isothermal period	0,2,4,6,8,16,20,30,40,60 min. steps or infinite	1-999 min. in 1 min. increments
Programme rates	10 linear rates: 0.5; 1; 2; 3; 4; 5; 7.5; 10; 15; 20°C/min.	1°C/min to 99°C/min in 1°C increments
Initial and final temperature settings	0°C - 450°C in 5°C steps	Ambient - 400°C in 1°C steps
Flow controls		
Carrier gas	Precision pressure regulator and gauge	Two adjustable metering valves standard Two flow control valves with direct reading rotometers optional
Detector (FPD)	United Analysts Company FPD	Meloy FPD
Detection limit	60 ppb	1 - 2 ppb
Output attenuator	1 - 1024 in binary steps	1 - 2048 in binary steps and a square root function, which linearizes the response from the detector
Ignition of hydrogen-rich flame	Manual	Automatic



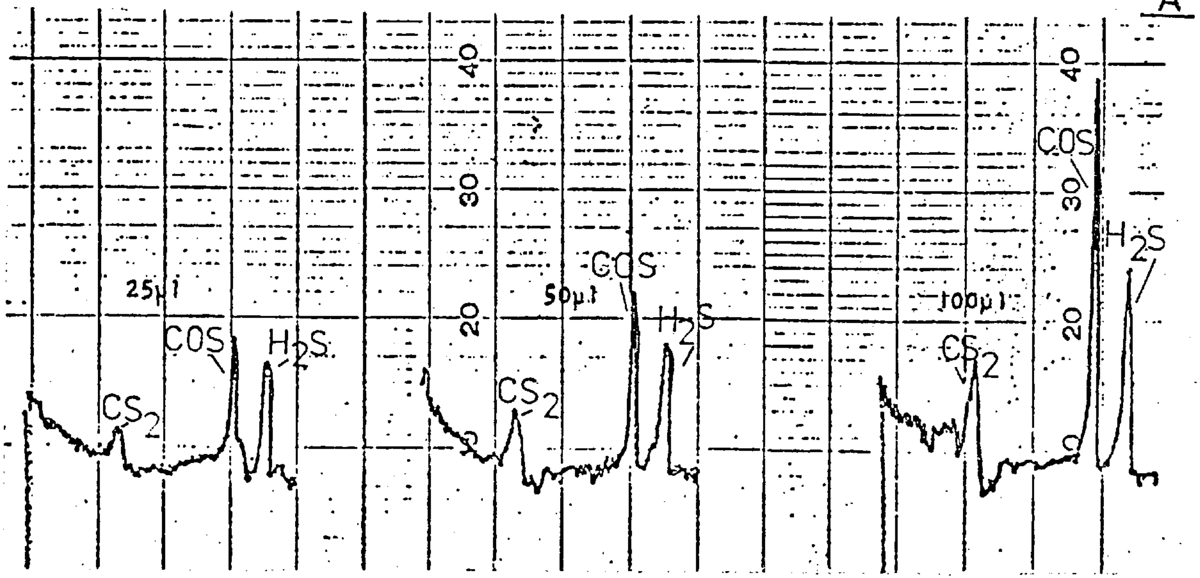


Fig. 6.11 Relative performance of the Tracor 560 (A) and the Perkin-Elmer F17 (B) gas chromatographs

6.4.3 Materials and Methods

The gas mixtures used to develop and evaluate the gas chromatographic methods were prepared in the laboratory by injecting small amounts of the test compounds such as hydrogen sulphide, sulphur dioxide, carbonyl sulphide, carbon disulphide, dimethyl sulphide and dimethyl disulphide into clean, graduated, 50 ml Sovirel glass bottles. These containers were sealed with a Teflon-lined rubber disc and a cap (through which a 2mm hole had been drilled to ensure that the gases only came into contact with glass and Teflon). Hamilton gastight hypodermic syringes of varying volumes were used when transferring a gas mixture from the Sovirel bottle to the chromatograph.

The columns used were of two types, one of which was made of Tracor special silica gel and packed in a silanized glass or Teflon tube. The other consisted of acetone-washed porapak QS* packed in an acetone-washed Teflon tube. The performances achieved with the columns mentioned are illustrated by Figs. 6.12 - 6.13. Recorder paper speed is 10mm/min in all chromatograms presented.

Different carrier gases such as argon, nitrogen, helium, carbon dioxide and hydrogen were used and tested. A molecular sieve filter, cooled in a container of solid carbon dioxide and isopropanol was used to further purify the "high purity" inert gases, which invariably gave peaks for carbon disulphide, (Fig. 6.18). The carrier gas was transferred from

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*Porapak QS is a silanized porous polymer composed of ethyl vinyl benzene cross-linked with divinyl benzene.

the gas cylinder to the flow controller and column in a Teflon tube, while the auxiliary gases such as air and oxygen were led from their cylinders in copper tubes as well as the hydrogen. Connectors as e.g. between the column and the injection port were always stainless steel with graphite, stainless steel or Teflon ferrules.

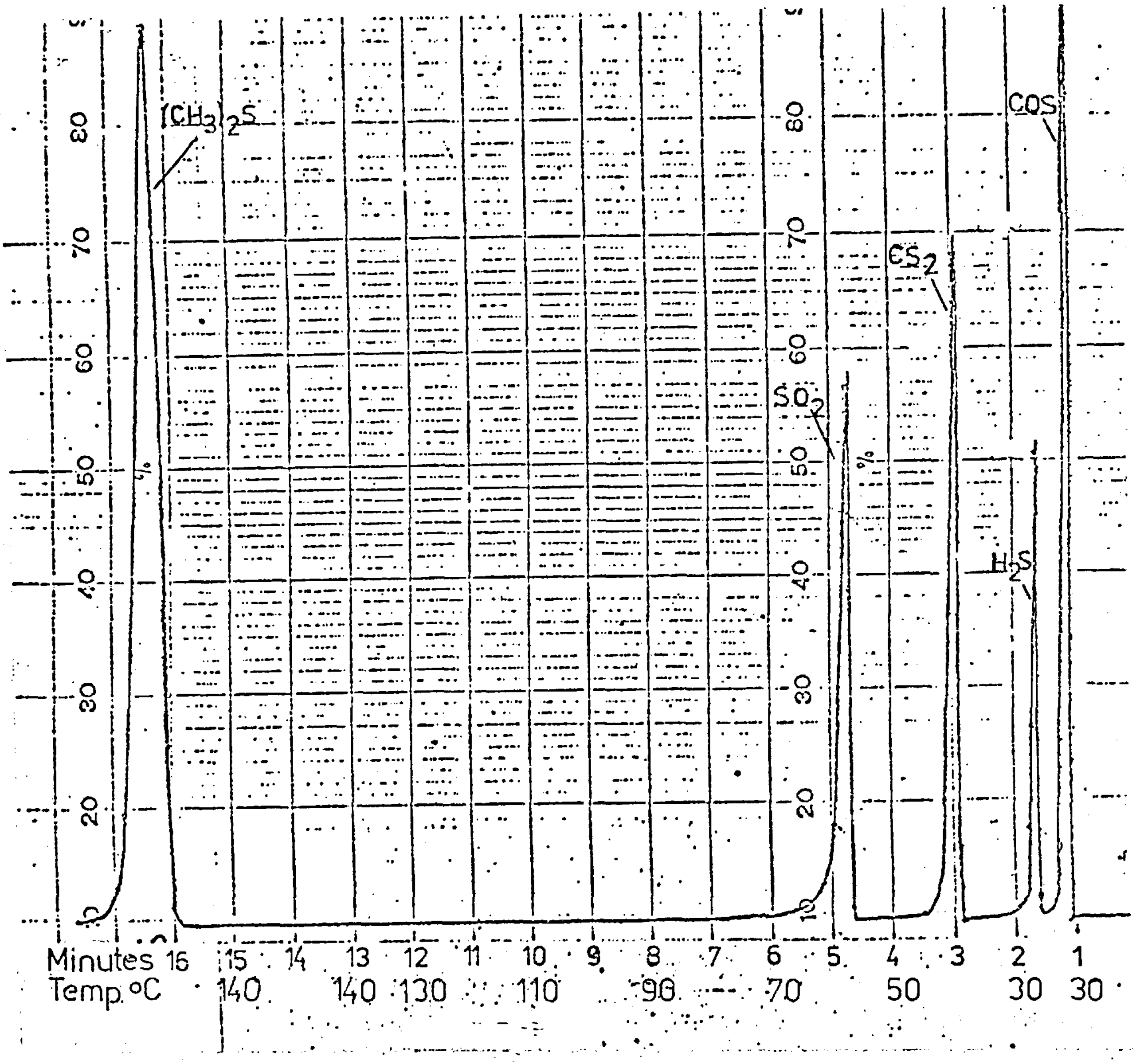

Fig. 6.12 Chromatogram obtained using a Tracor special silica gel column operated between 30-140°C with a heating rate of 10°C/min after an initial temperature hold for 2 minutes.

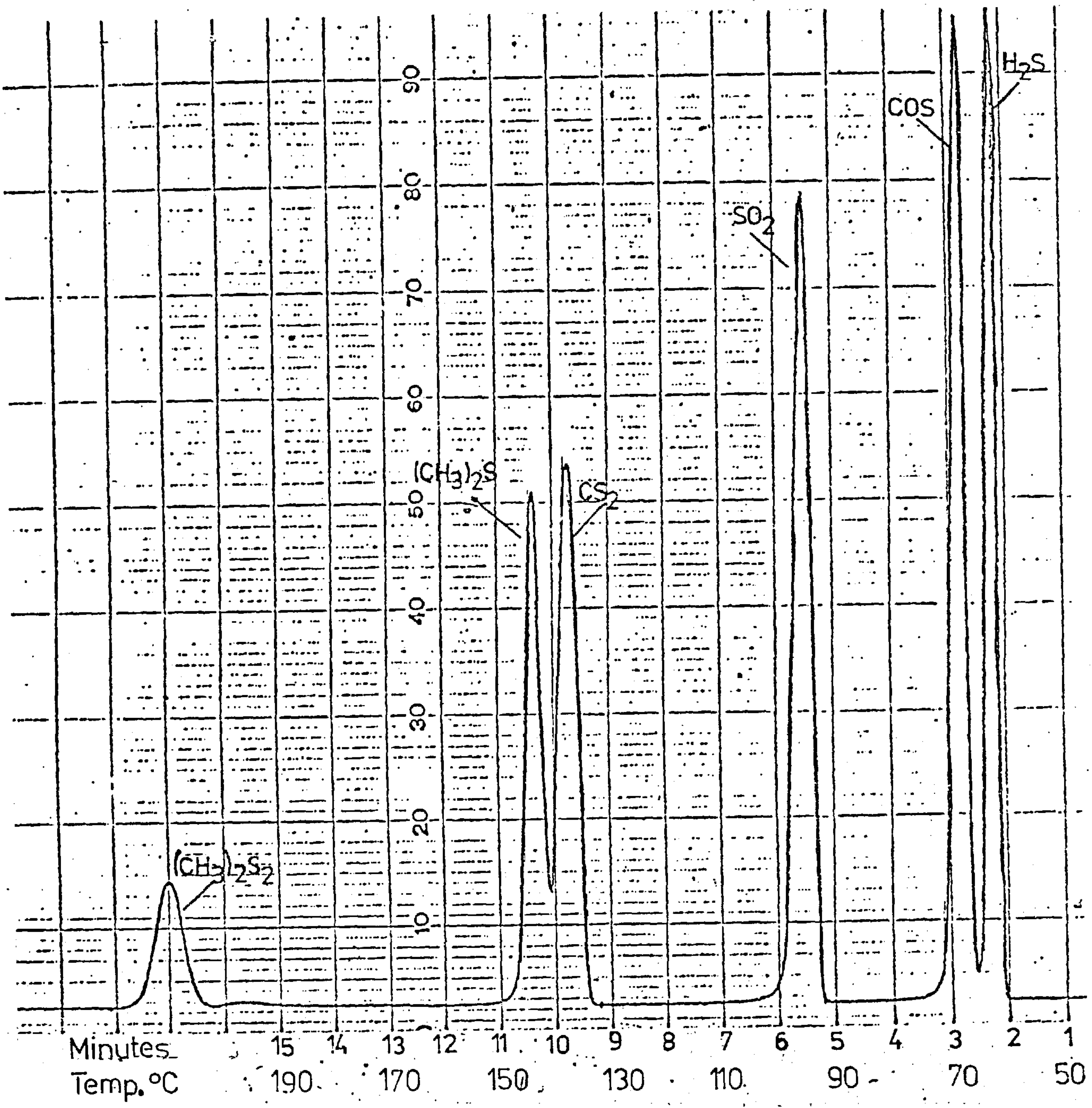

Fig. 6.13 Chromatogram obtained using acetone-washed Porapak QS column operated between 50°C-190°C with a heating rate of 10°C/min after an initial holding of 50°C for 1 minute (column after conditioning)

Columns

The resolution of carbonyl sulphide from hydrogen sulphide and carbon disulphide from dimethyl sulphide on one column has been proved to be extremely difficult due to factors such as tailing, adsorption on column walls and packing, close retention time of the components under the conditions used, etc.. The resolution of all four gases on a single column is especially difficult. After many trials with different column packings such as silica gel, Tracor special silica gel and Porapak QS, the two latter proved to be the best overall for the requirements needed (silanized glass and Teflon columns were used). Satisfactory separations were obtained by both packings (Fig. 6.12 - 6.13). Of the two packings, the Porapak QS has been found to be the best due to the fact that it is not seriously affected by moisture developed in the system when desorbing the adsorption tubes (as described below) since the water quickly passes through the column and therefore does not interfere with following peaks. Dimethyl disulphide is permanently absorbed by Tracor special silica gel, while in columns packed with Porapak QS it is eluted after about 17 minutes. Table 6.2 gives information on physical and chemical properties of some sulphur gases as well as the retention times obtained on columns packed with either Porapak QS or Tracor special silica gel.

The length and the packing density of the column affect the separation of gases as illustrated in Figs. 6.14 - 6.16. A poor separation of hydrogen sulphide and carbonyl sulphide is obtained when using a 57 cm long acetone-washed Porapak QS. The separation of these two components is improved by using

Table 6.2 Properties of low molecular weight sulphur compounds (partly from Lange's handbook of Chemistry, 1973)

Gas	Molecular weight	Boiling point (°C)	Specific gravity	Retention time (sec)	
				Tracor/Special Acetone-washed	silica gel/ Porapak QS
Sulphur dioxide, SO_2	64	-10	1.4337	294	348
Hydrogen sulphide, H_2S	34	-60.2	1.1895	102	144
Carbonyl sulphide, COS	60	-50.2	2.105	72	178
Carbon disulphide, CS_2	76	46.3	1.260	186	588
Methyl mercaptan, CH_3SH	48	5.96	0.896		
Dimethyl sulphide, $(CH_3)_2S$	62	37.3	0.845	990	630
Dimethyl disulphide, $(CH_3)_2S_2$	94	34.6	71.26		1020

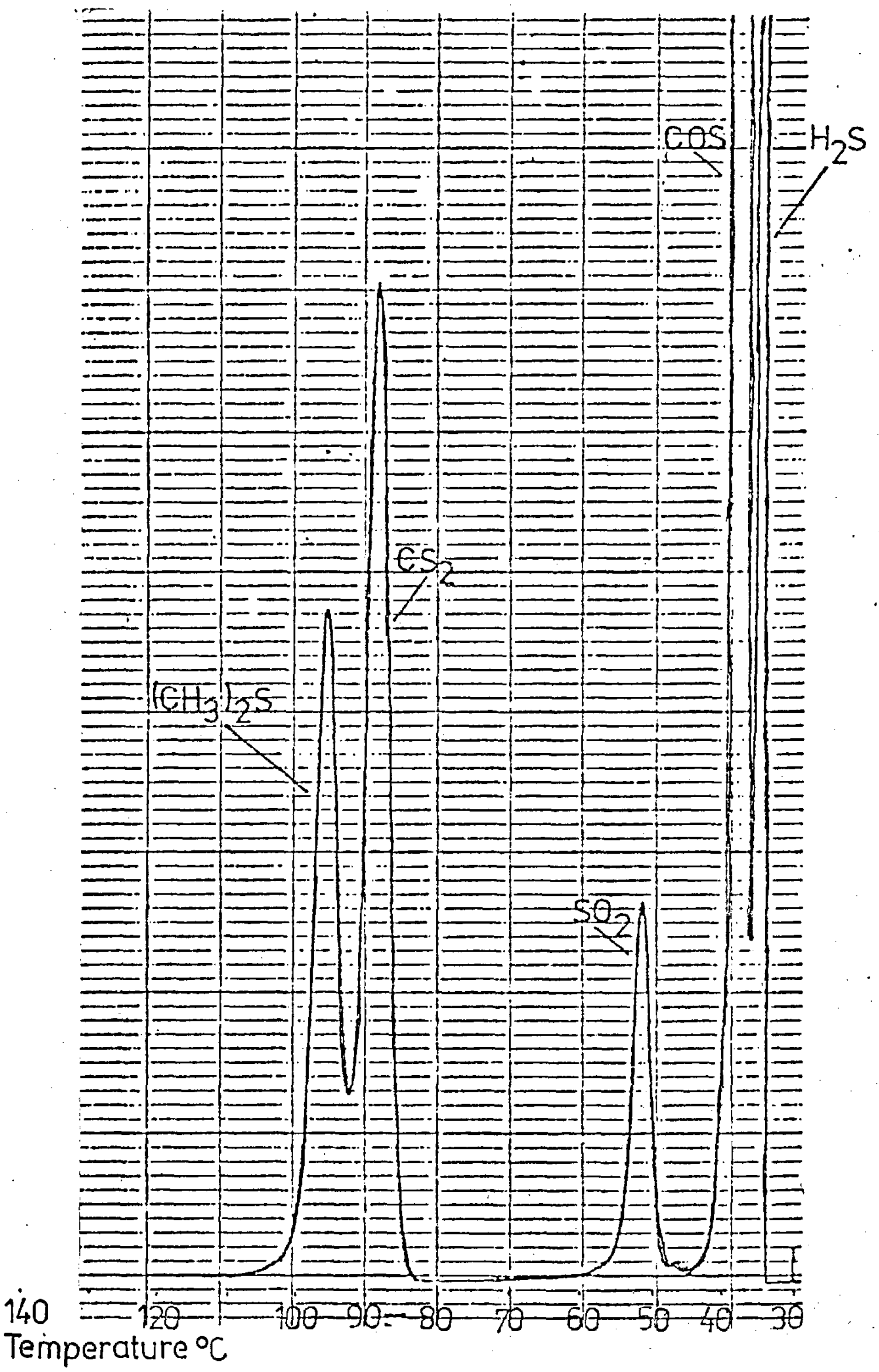

Fig. 6.14 57cm long Porapak QS column showing poor resolution between H_2S and COS (Temperature 30-140°C).

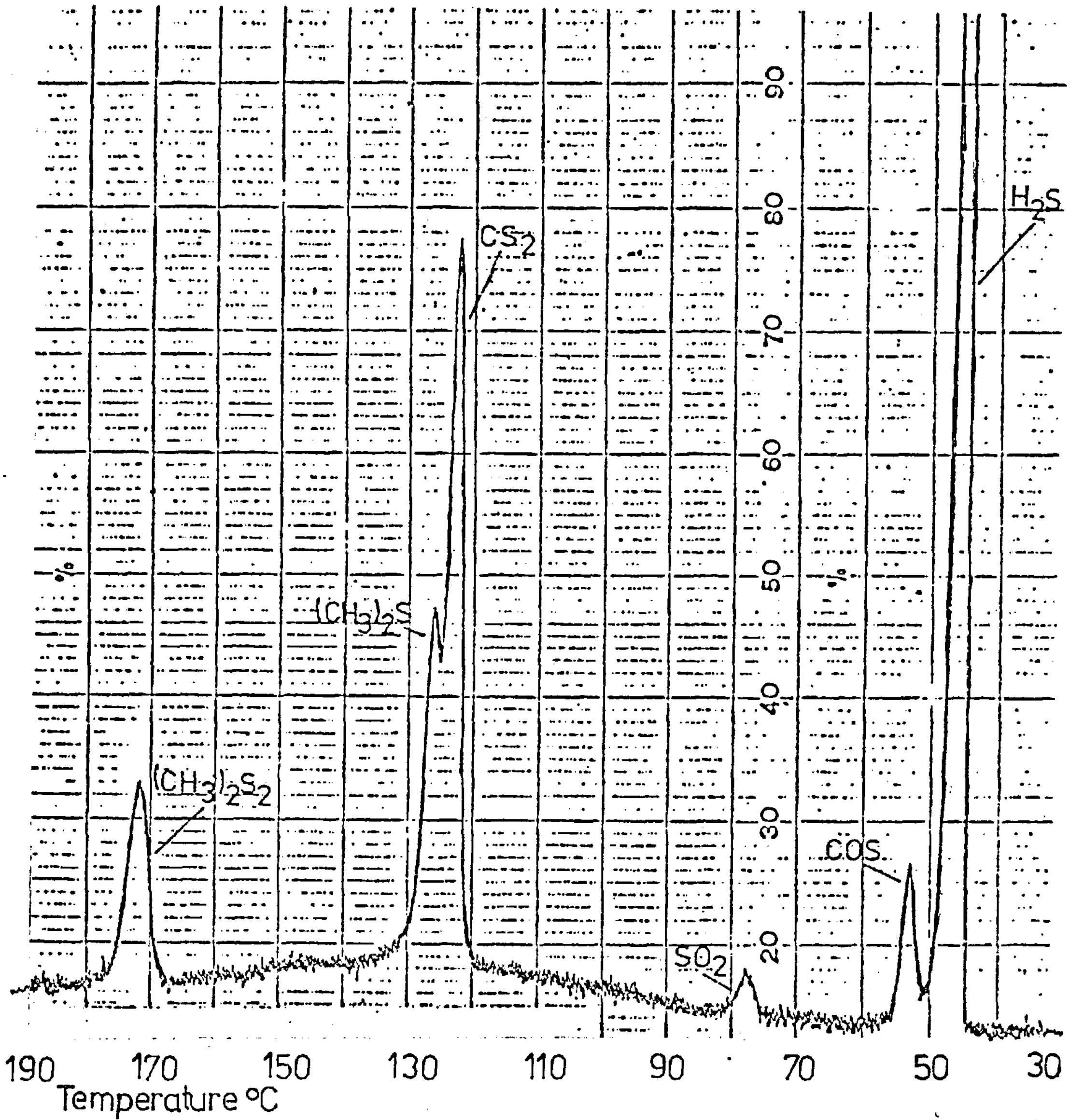

Fig. 6.15 98 cm long Porapak QS column showing improved resolution between H_2S and COS, but poor resolution between CS_2 and $(CH_3)_2S$ (Temperature 30-190°C).

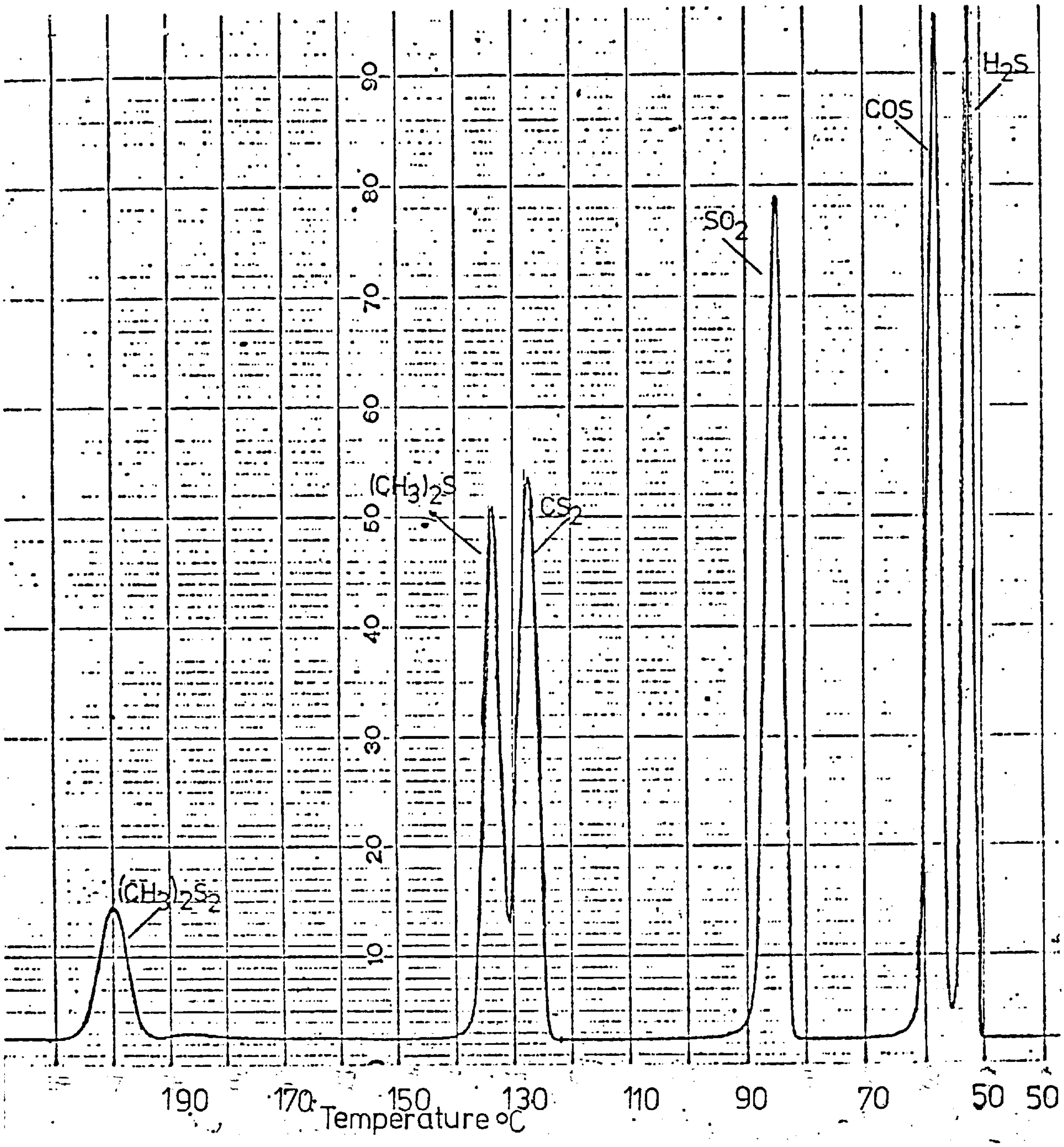

Fig. 6.16 150 cm long Porapak QS column operated between 50-190°C with good separation of all gases.

a 98 cm long column, but the separation of carbon disulphide and dimethyl sulphide has become poor probably depending on a too low packing density in the column. A 150 cm long column shows an overall satisfactory separation of hydrogen sulphide, carbonyl sulphide, sulphur dioxide, carbon disulphide, dimethyl disulphide and dimethyl disulphide.

Column preparation

Teflon (PTFE) and Porapak QS were selected as the most suitable column material and packing, respectively, due to their non-adsorptive properties to sulphur gases. Adsorption between column walls, packings and sulphur gases has been reported in the literature (Stevens et al, 1971) as being one of the major factors preventing quantitative analysis of sulphur gases below 1 ppm.

When packing a column, an acetone-washed Teflon tube was plugged at one end with silanized glasswool and held vertically. A modified 25 ml pipette, filled with acetone-washed 80/100 mesh Porapak QS, was employed to fill the column, by a vibration technique. The Porapak QS was transferred in small aliquots to ⅛-inch inner diameter Teflon tubes of varying lengths (40 - 180 cm) with the aid of an electrical vibrator and a vacuum pump. After filling the tube uniformly, the open end was sealed with silanized glasswool.

The method of washing the Porapak QS for obtaining satisfactory separation of sulphur gases is critical. A few grams of 80/100 mesh Porapak QS, contained in a Buchner funnel with a fine porosity glass-frit bottom, is washed with chemically pure acetone under suction for 5 - 10 minutes. When the column packing is completely dry, it is ready for use. Souza et al (1975) showed the difference in performances on acetone-washed and untreated Porapak QS respectively (Fig. 6.17).

Column conditioning and stabilization

The acetone-washed Porapak QS packed columns were conditioned overnight in the gas chromatographic oven. The temperature was held at 30°C for the first hour and thereafter was increased to 220°C using an increment of 5°C/min. An argon carrier gasflow of 50 ml/min was maintained through the column which was disconnected from the detector. Immediately after conditioning, an erratic baseline and poor resolution between the components were noticed (Fig. 6.18). However after such a column has been in use for a period of time its performance improves with the result that the gases can be separated from each other. The separation of the gaseous compounds and stabilization of the baseline were also improved by injecting sulphur gases in the column several times. A good performance was obtained after these repetitive injections of sulphur volatiles due to the saturation with sulphur gases of adsorption sites on column walls and packing. Negative peaks, indicating the presence of hydrocarbons were also observed on new columns (Fig. 6.19). These peaks tend to disappear with increasing use of columns (Fig. 6.13).

Standard gas samples

Gas mixtures of approximate composition were prepared following the method described in Section 6.4.3. If

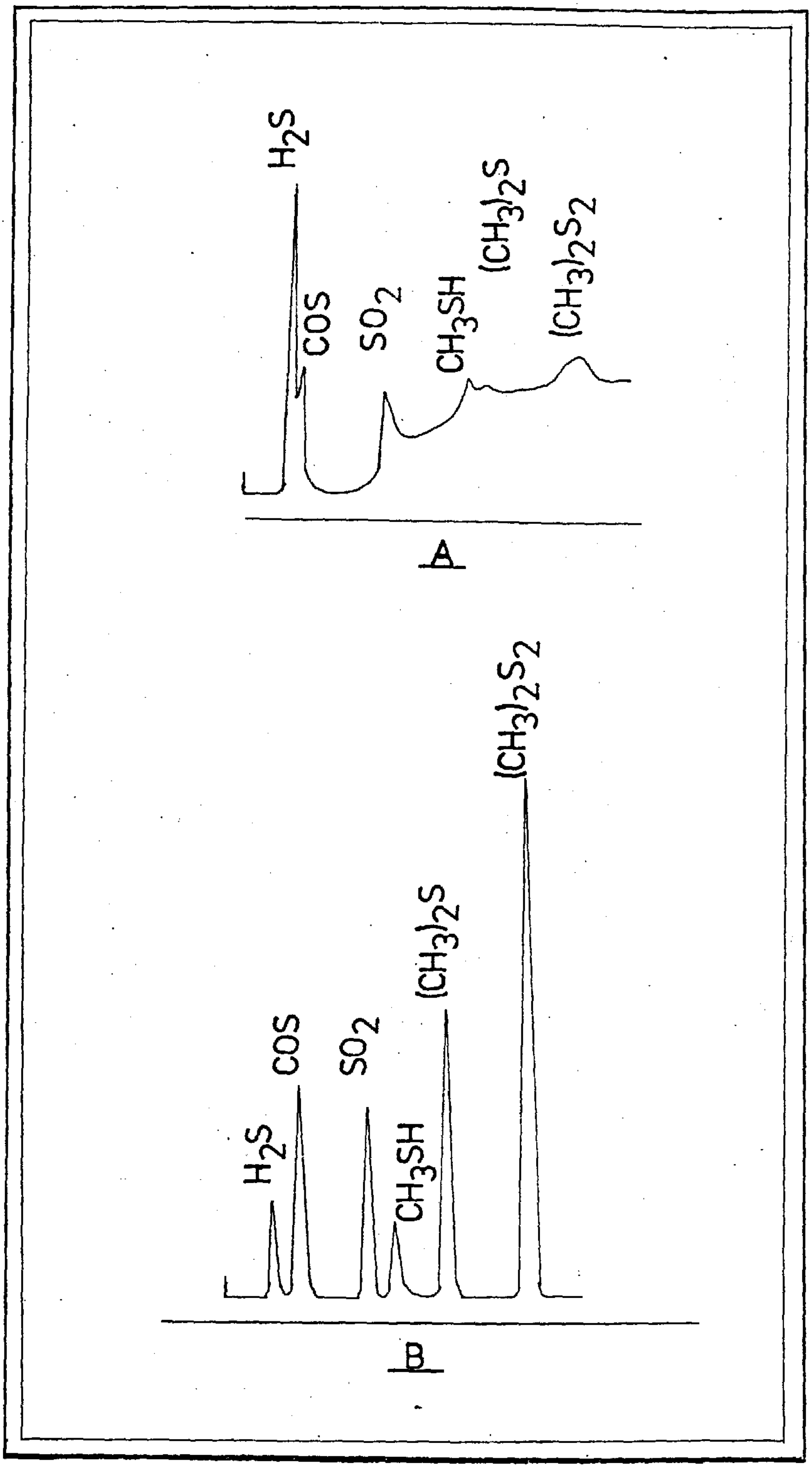

Fig. 6.17 A Chromatogram obtained with untreated Porapak QS.

B Chromatogram obtained with acetone-washed Porapak QS

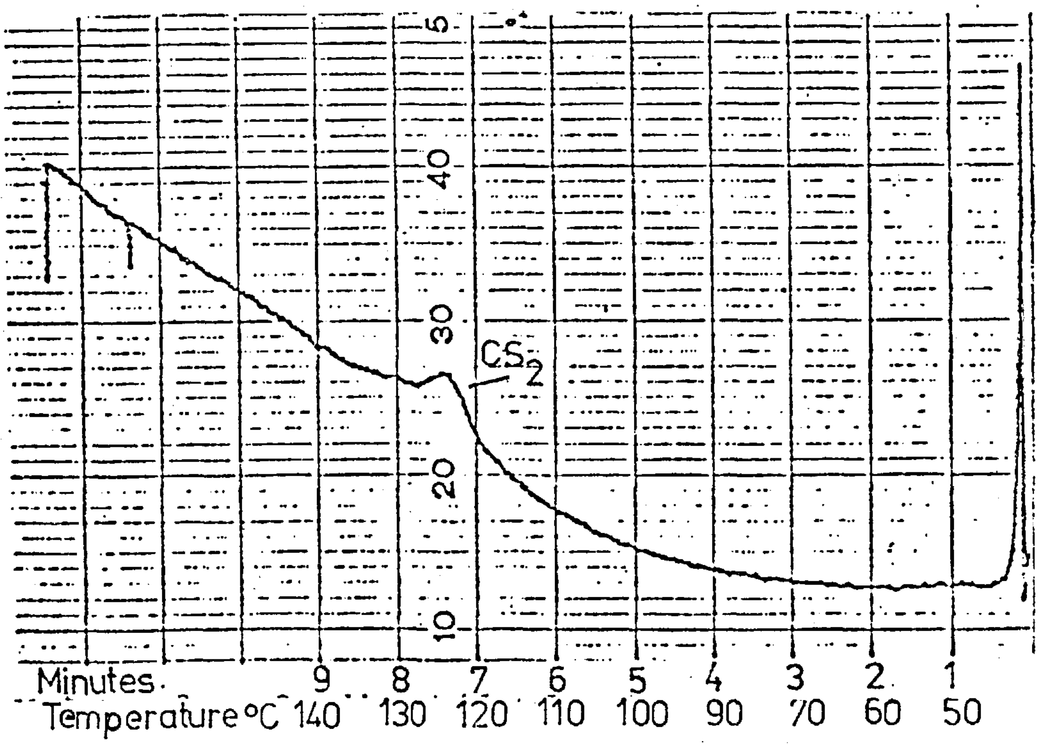

Fig. 6.18 Baseline drift of freshly prepared acetone-washed Porapak QS column with peak for CS_2

necessary, the gas mixture samples were diluted in another Sovirel bottle before presentation to the chromatograph. Aging of the gas mixtures was noted resulting in a change of composition; sulphur dioxide and hydrogen sulphide reacting with each other:

$$SO_2 + 2H_2S \rightarrow 2H_2O + 3S$$

In preparing the gas mixture, headspace gas samples were taken from those sulphur gases which are liquid at room temperature (carbon disulphide, dimethyl sulphide and dimethyl disulphide). Sulphur dioxide was obtained from a 250 ml gas cylinder and was liquified by cooling to about -75°C using solid carbon dioxide. The headspace gas over the resulting liquid was then sampled. Hydrogen sulphide was prepared by adding concentrated sulphuric acid to sodium sulphide. Finally, carbonyl sulphide was obtained by adding sulphuric acid (5:4; H_2SO_4: H_2O) to ammonium thiocyanate. A chromatogram showing separation of all six sulphur gases (sulphur dioxide, hydrogen sulphide, carbon disulphide, carbonyl sulphide, dimethyl sulphide and dimethyl disulphide) is illustrated in Fig. 6.20. The retention time of each individual component was determined by stepwise addition of the different sulphur gases to the Sovirel bottle followed by analysis.

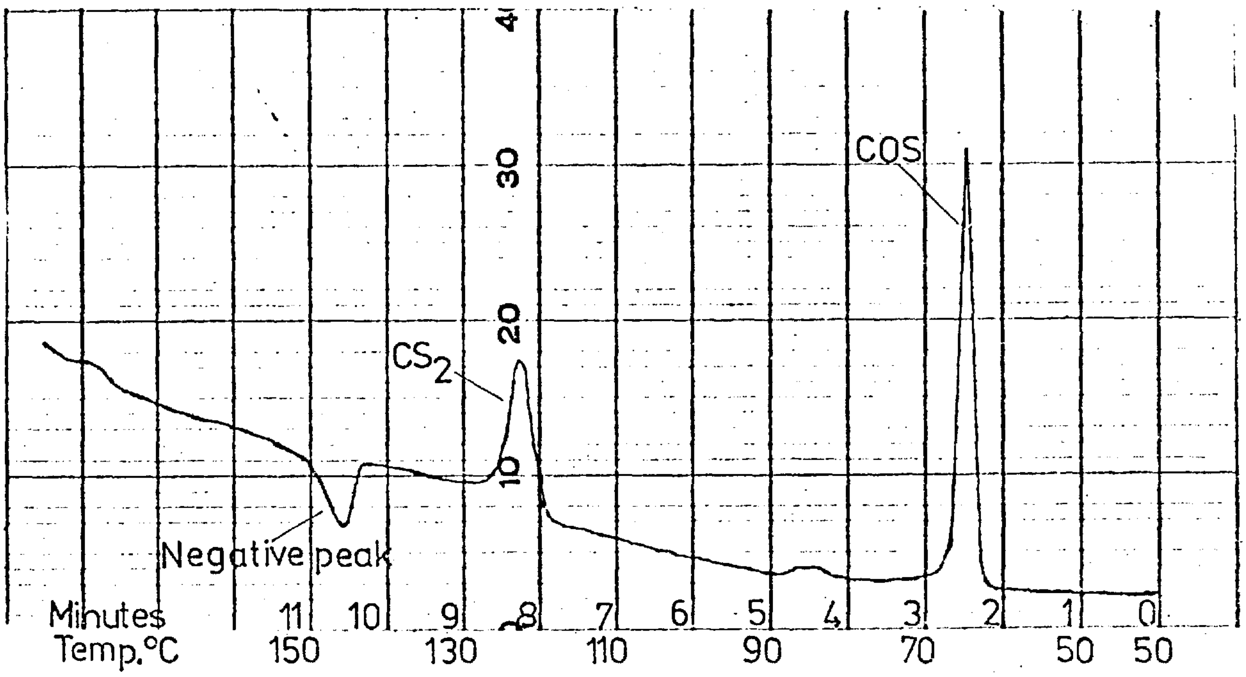

Fig. 6.19 Chromatogram showing a negative peak, due to the presence of hydrocarbons, and baseline drift on freshly prepared Porapak QS column.

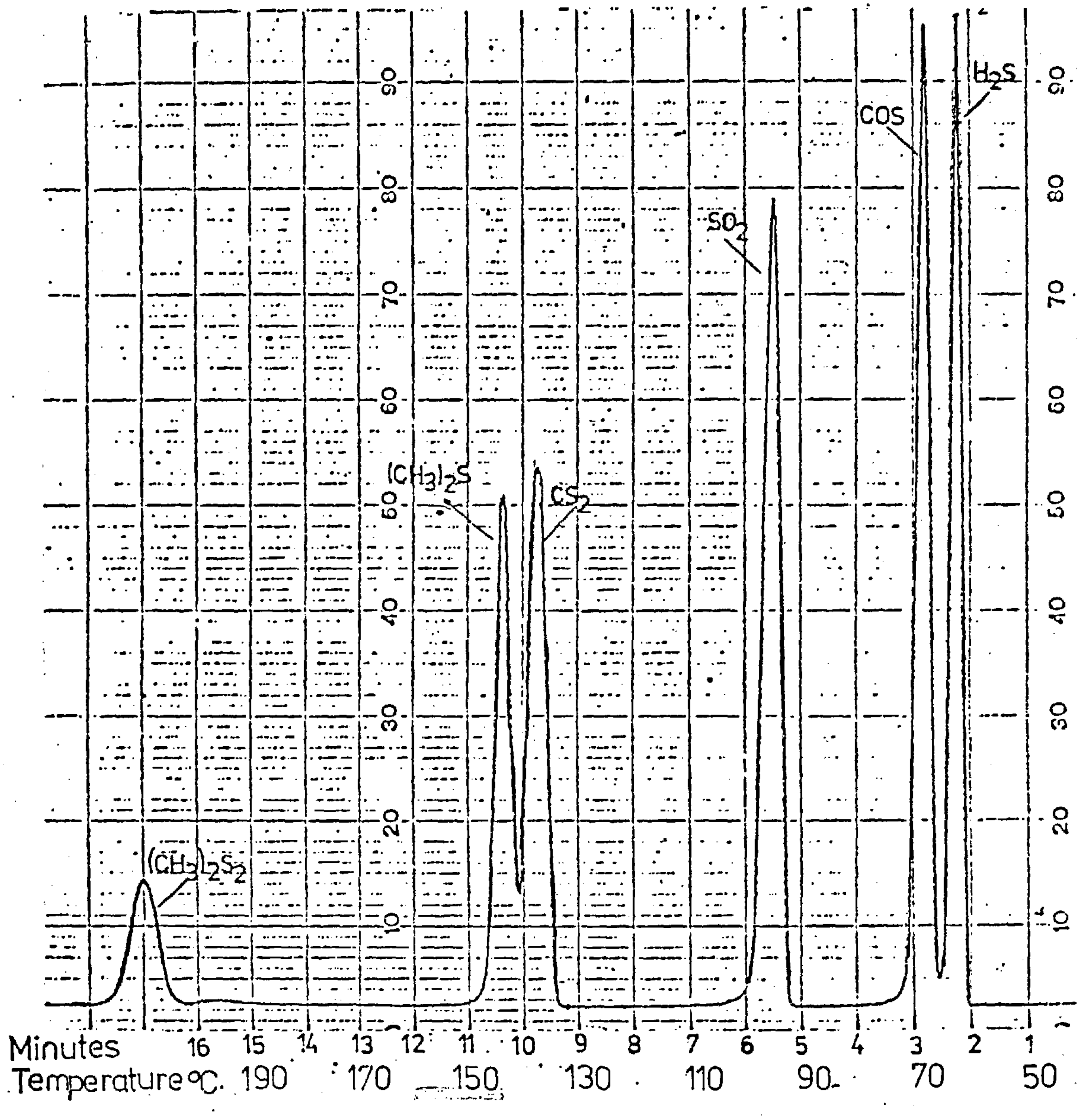

Fig. 6.20 Chromatogram showing separation of the components of a gas mixture using a Porapak QS column.

Carrier gases

Many different "high purity" inert gases were used as carrier gas. As mentioned elsewhere, the carrier gas was further purified by molecular sieve, immersed in a container of solid carbon dioxide and iso-propanol, before passing through the column. The effects of argon, carbon dioxide, helium nitrogen and hydrogen were investigated. Carbon dioxide gave a poor response and an erratic baseline. Ronkainen et al (1973) state that carbon dioxide causes response on the flame photometric detector, when present in high concentrations. The other four gases all gave good responses and stable baselines (Fig. 6.21 - 6.23). Argon was finally chosen as the carrier gas due to its stated high separating power. Although Fig. 6.22 - 6.23 show that helium and nitrogen could be used as well, since the separation of the different components is good.

Oven temperature

The oven temperature affects the resolution of gases during chromatography. For example Fig. 6.24 shows the improvement in resolution between sulphur dioxide and carbonyl sulphide or hydrogen sulphide brought about by reducing the oven temperature from 80°C - 70°C. Without the facility to programme the oven temperature separation of both low molecular weight inorganic sulphur gases from the later organic compounds would have been impossible. Temperature programming was therefore used for all chromatograms illustrated in this thesis.

Operational procedure

The conditions presented below have been used with minor changes, to obtain chromatograms such as those illustrated

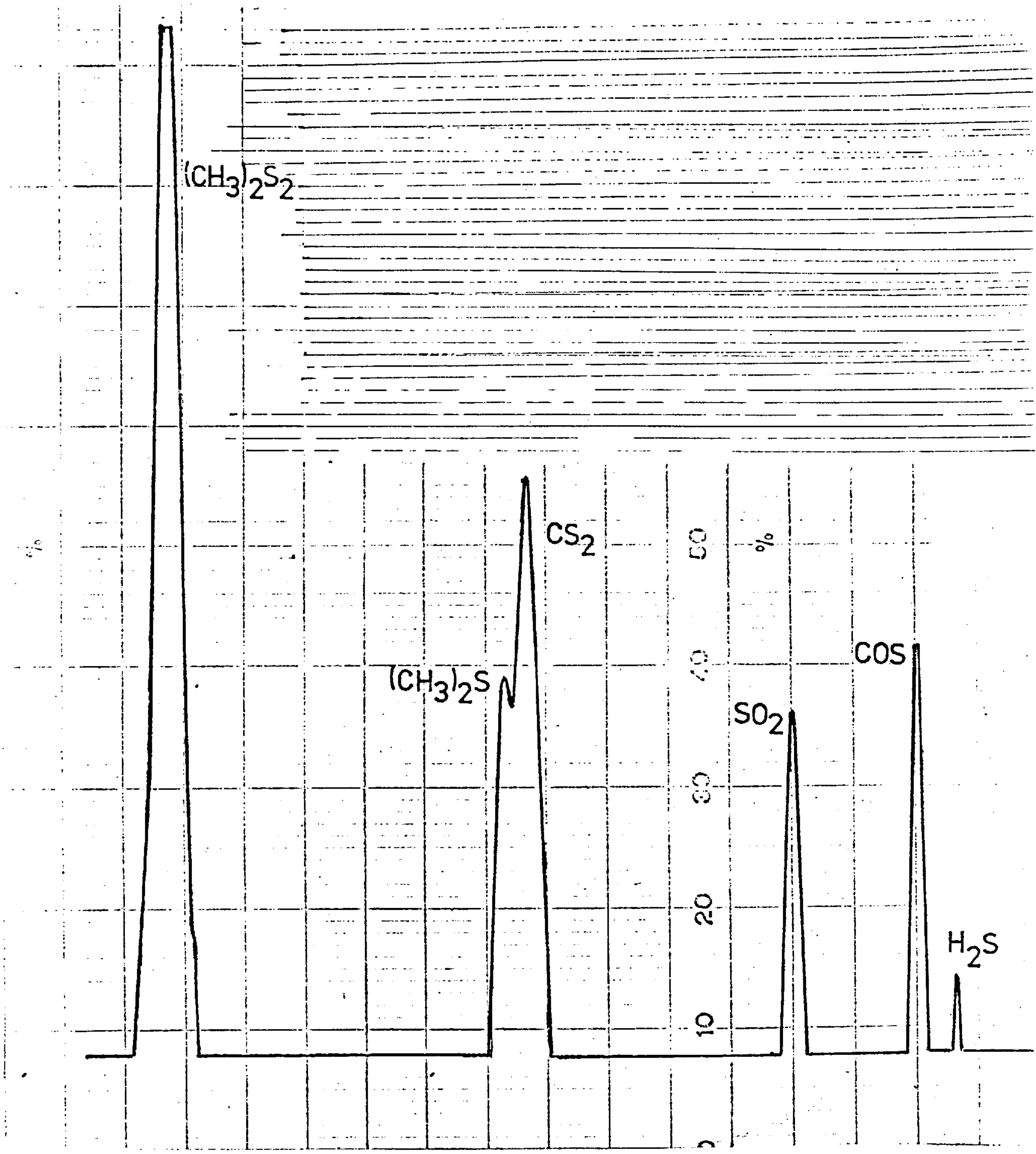

Fig. 6.21 Chromatogram showing separation of sulphur gases using argon as the carrier gas (50 - 170°C, 10°C/min)

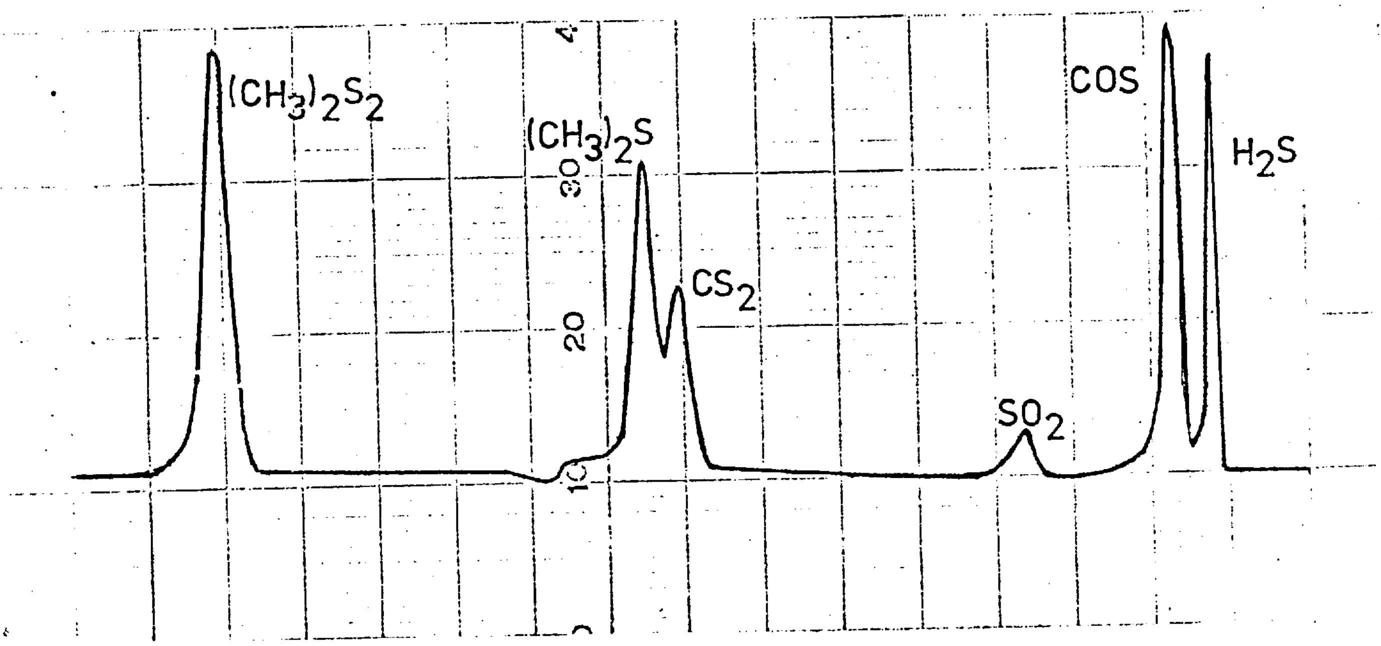

Fig. 6.22 Chromatogram showing separation of sulphur gases using helium as the carrier gas (50 - 170°C, 10°C/min)

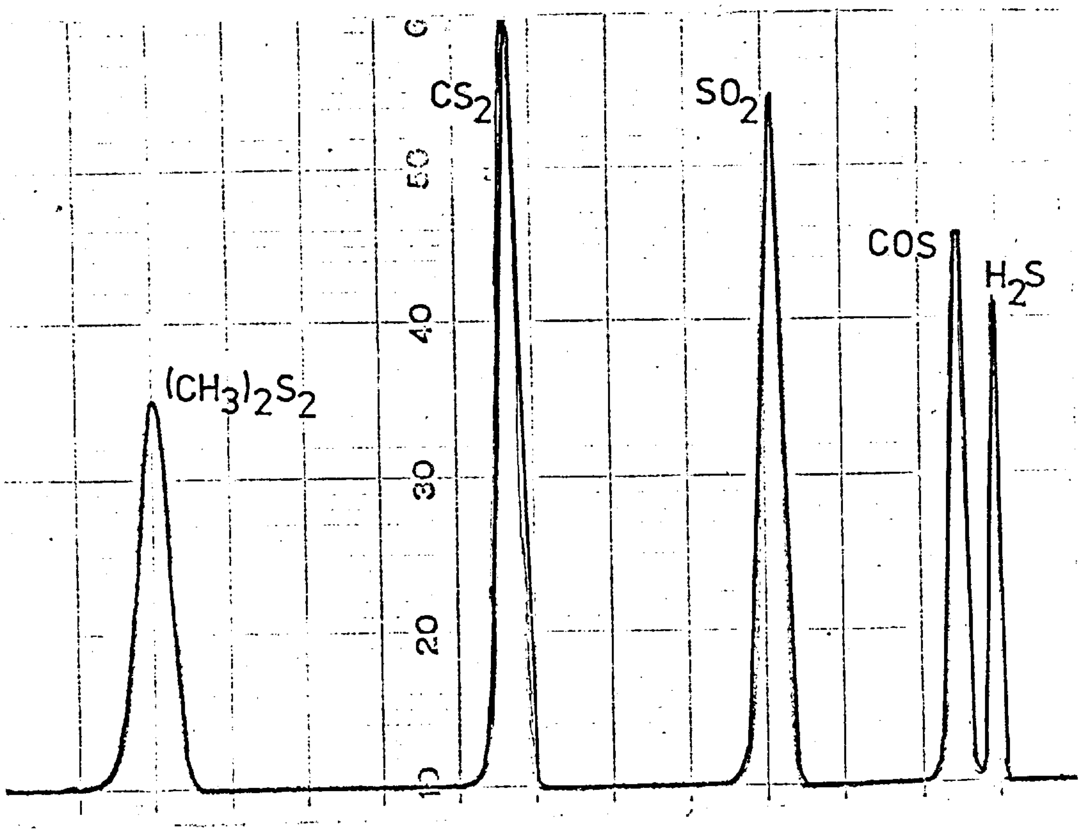

Fig. 6.23 Chromatogram showing separation of sulphur gases using nitrogen as the carrier gas (30°-140°C, 15°C/min)

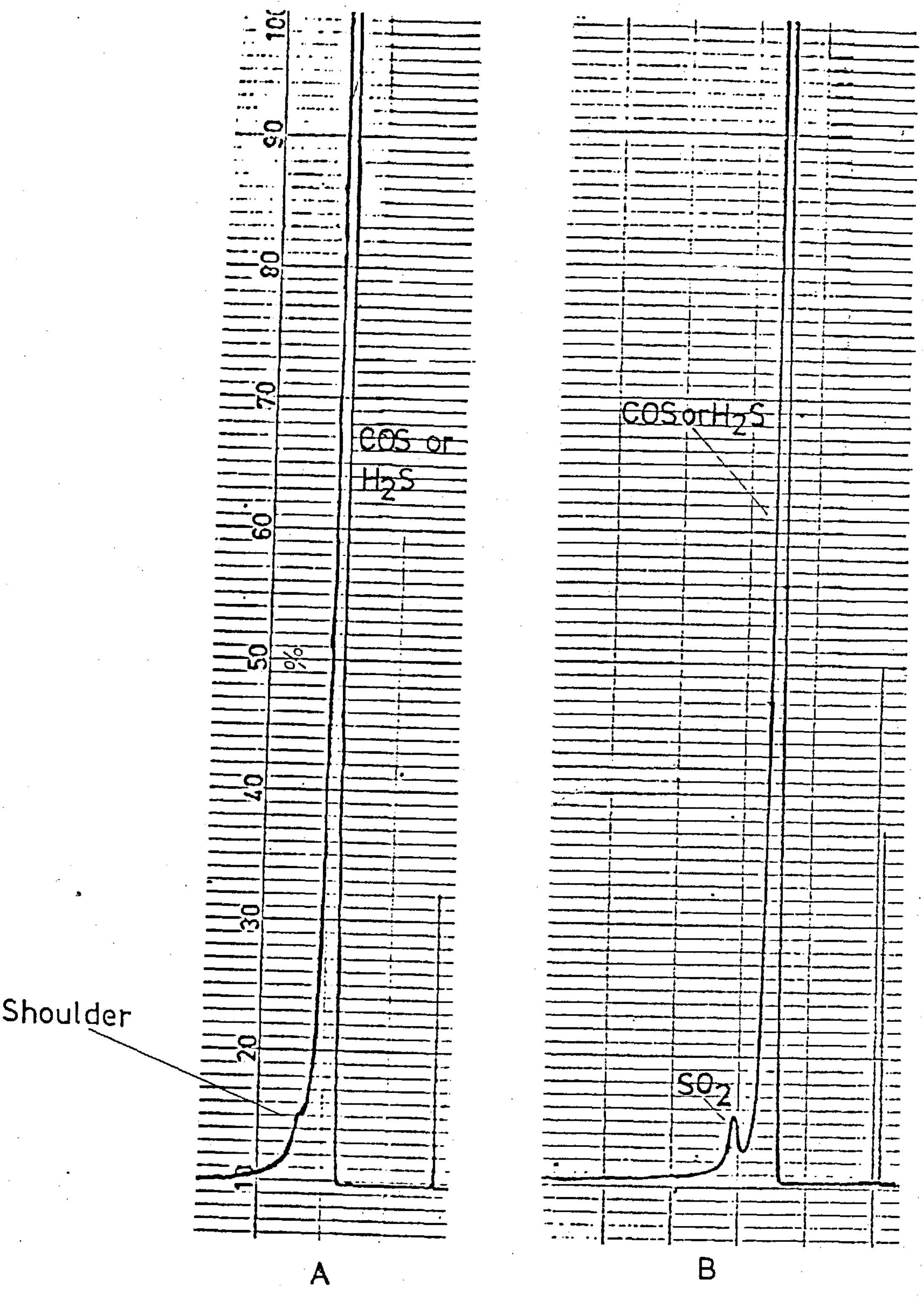

Fig. 6.24 Part of a chromatogram obtained on the analysis of the headspace over Parys Mountain Sulphides

A - Temperature 80°C. Only a "shoulder" can be seen on the main peak for COS or H_2S

B - Temperature 70°C. Resolution has been improved showing a distinct peak for SO_2

in the following part of this thesis, since these have been found to be the most suitable in the analysis of a sulphur gas mixture of hydrogen sulphide, carbonyl sulphide, sulphur dioxide, carbon disulphide, dimethyl sulphide and dimethyl disulphide in the low ppb range.

Table 6.3 Operational conditions for gas shromatographic analysis of sulphur-bearing gas mixtures using an acetone-washed Porapak QS column

Column temperature	Programmed, start 50°C, initial temperature hold for 1 or 2 min. to 170°C at a temperature rate of 10°C/min. Final temperature hold for 5 minutes, followed by cooling of the oven to 50°C.
Carrier gas	Argon at 50 - 100 ml/min. The flow-rate does not affect the performance when temperature programming is used.
Sample volume	1 - 5 ml
Detector temperature	200°C
Detector port temperature	80°C
Detector gases	
Air	90 ml/min
H_2	60 ml/min
Chart speed	10 ml/min

6.4.4 Analysis of Headspace Gas over Natural Sulphide Samples

In the preliminary gas chromatographic analysis of the headspace over sulphides (enclosed in Sovirel glass bottles) two unknown sulphur volatiles were detected (Figs. 6.8 - 6.10). Later experiments with sulphur gases, evolved from oxidizing sulphides under laboratory conditions have shown that the major peaks are due to carbon disulphide and carbonyl sulphide (Fig. 6.25). Neither hydrogen sulphide nor sulphur dioxide have been detected in large quantities, if at all. The latter compound was in fact only detected over freshly crushed pyrite, which also produced carbon disulphide (Fig. 6.26). Freshly crushed galena, on the other hand, mostly gave off carbonyl sulphide and carbon disulphide (Fig. 6.9). Dimethyl disulphide has been detected only in the headspace gas over wet Parys Mountain sulphides (pyrite, galena, sphalerite and oxidized copper minerals) (Figs. 6.27 - 6.28) which also produced small quantities of sulphur dioxide (Fig. 6.27).

Gas chromatographic analysis of the sulphur gases liberated by oxidizing sulphides under laboratory conditions were compared and identified with the aid of retention times of reference standard gases. In the experiments, wet sulphides were found to produce more sulphur gases than dry samples (Figs. 6.27 - 6.30). It was further noticed that the concentrations in the headspace gas in the glass bottles declined rapidly with time unless large amounts of sulphides were present (Figs. 6.25 - 6.28 and 6.31). The change of composition in the gas mixtures with time was mentioned on p.168.

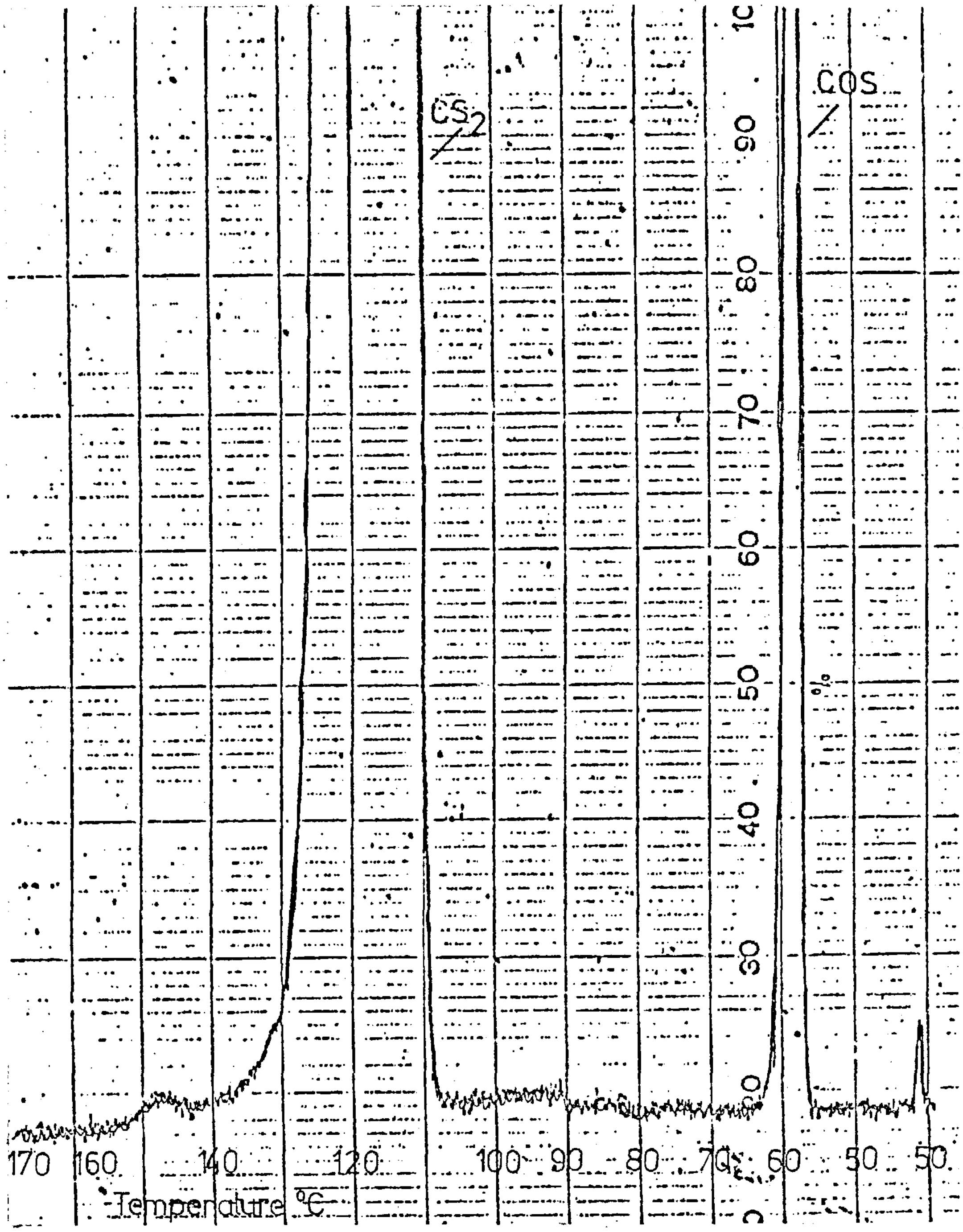

Fig. 6.25 Chromatogram of headspace gas over crushed, wet Trefriw pyrite after 6 weeks in a closed bottle showing high concentrations of vapours.

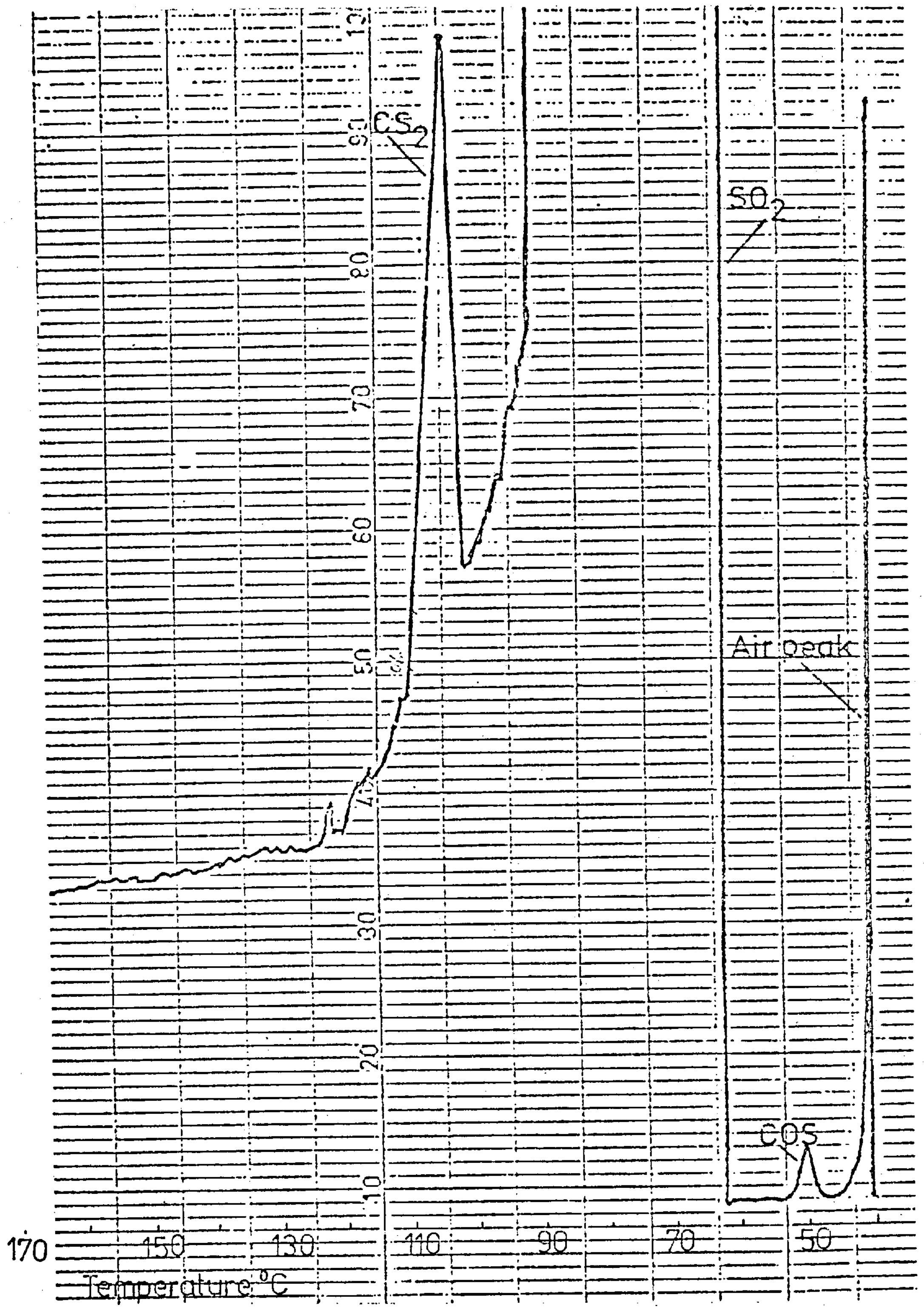

Fig. 6.26 Chromatogram illustrating sulphur dioxide, derived from freshly crushed Trefiw pyrite.

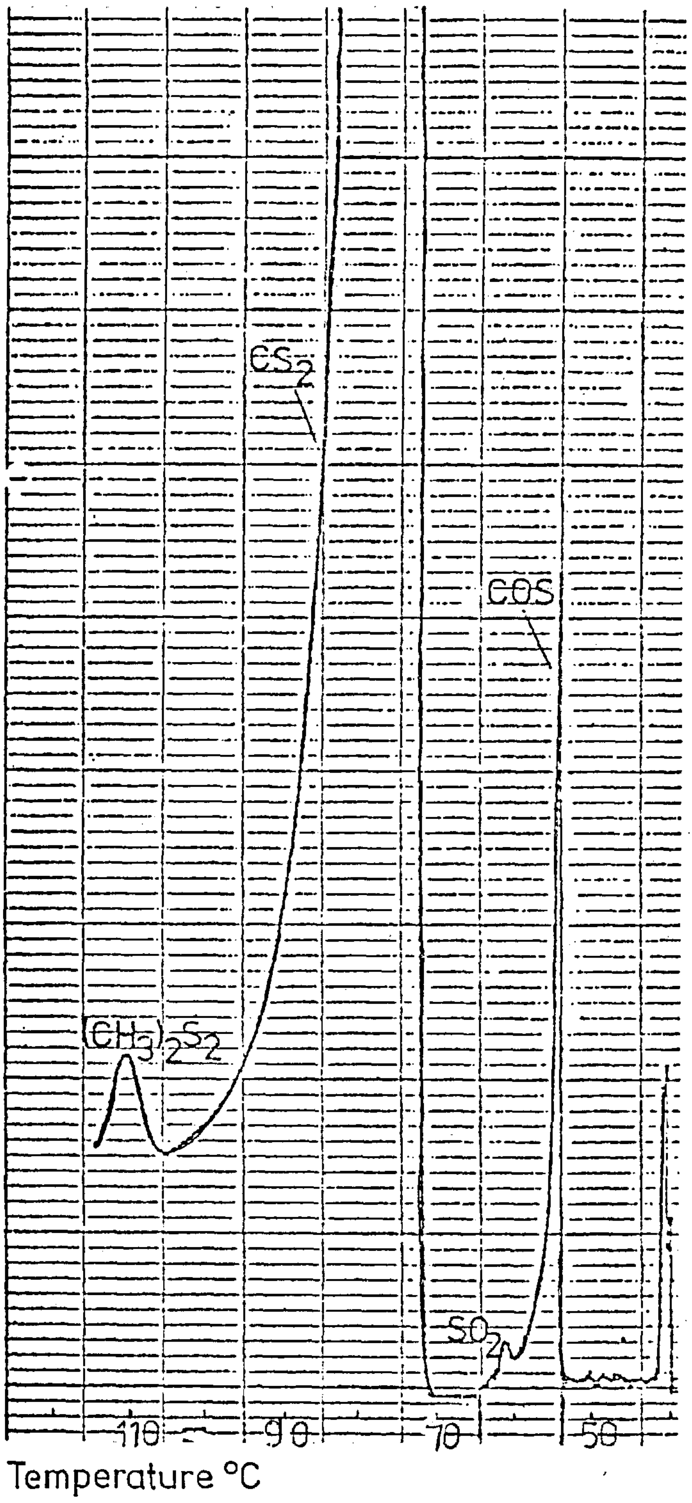

Fig. 6.27 Chromatogram of headspace gas over wet Parys Mountain sulphides.

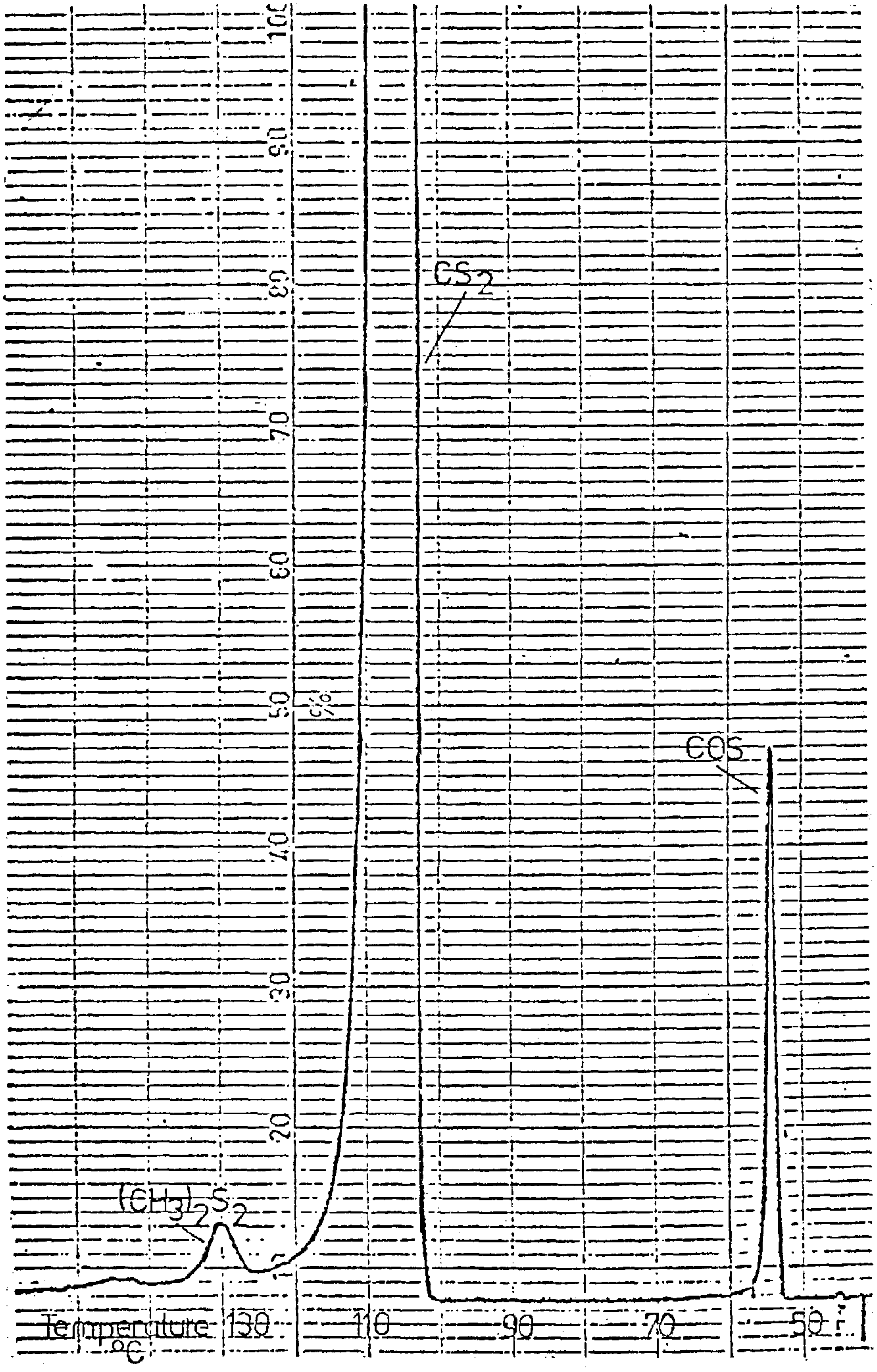

Fig. 6.28 Chromatogram of headspace gas over wet sulphides from Parys Mountain after six weeks storage.

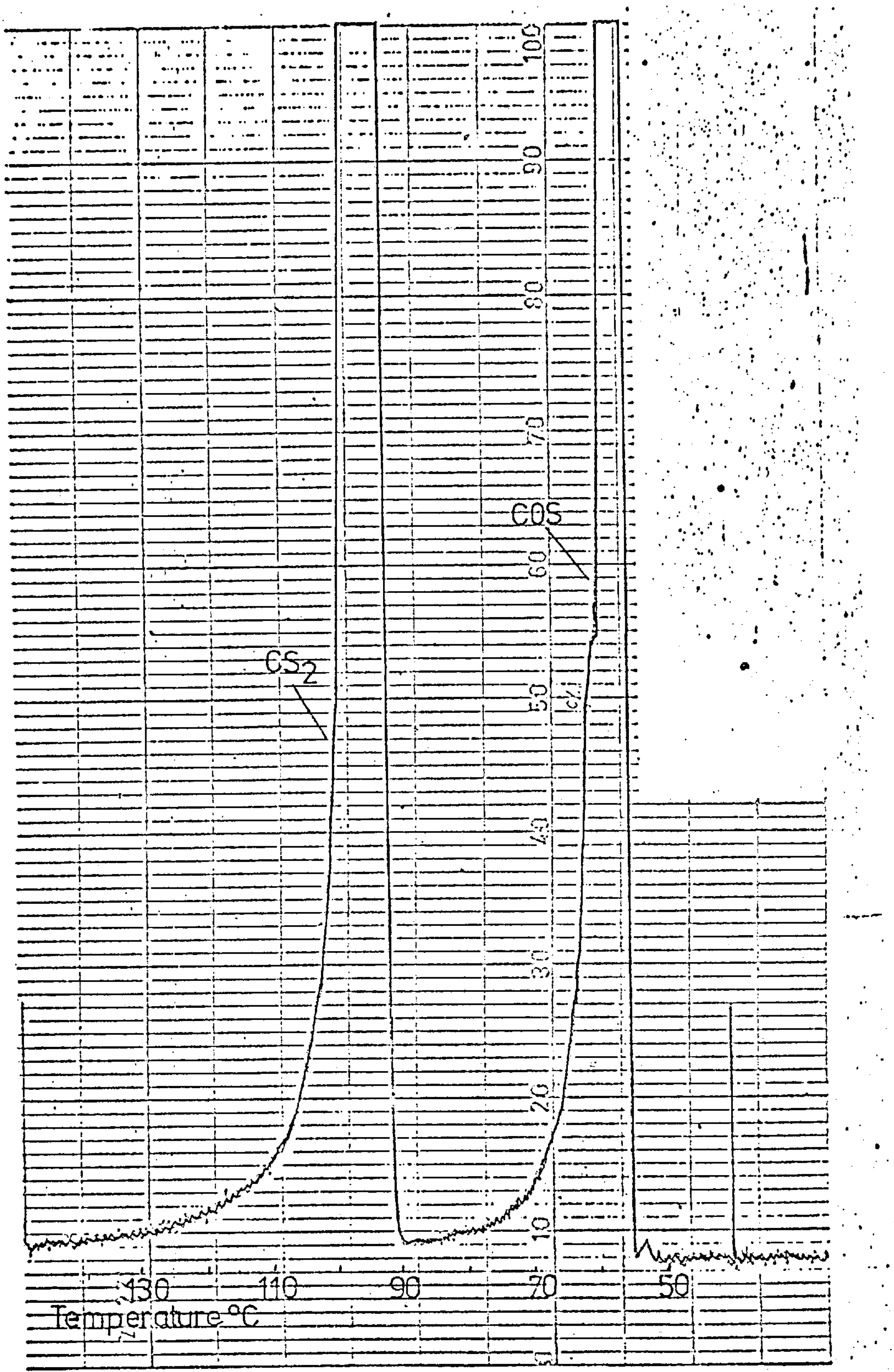

Fig. 6.29 Chromatogram of headspace gas over dry Parys Mountain sulphide sample.

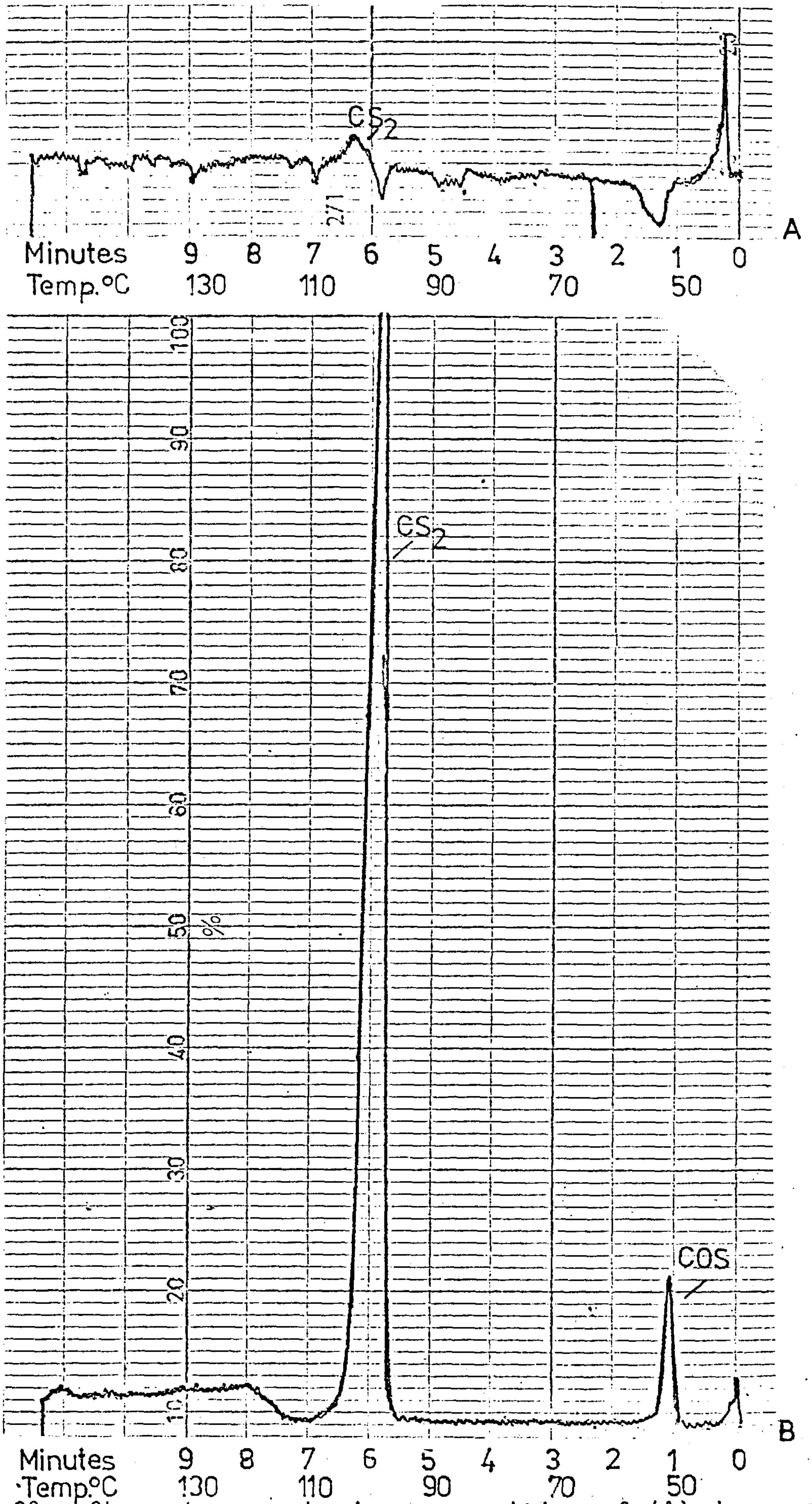

Fig. 6.30 Chromatogram showing composition of (A) dry and (B) wet sample from a Rodalquilar dump.

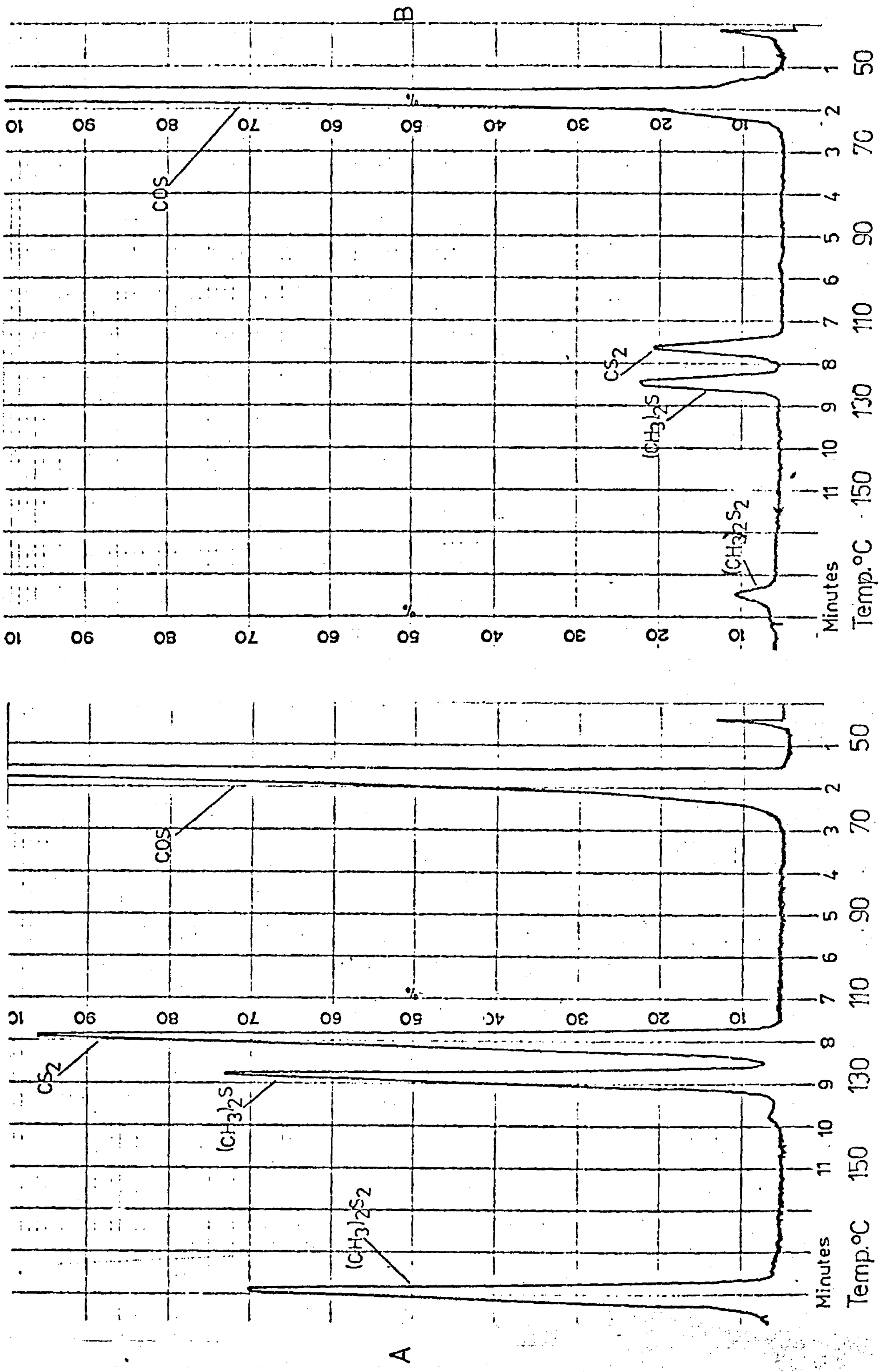

Fig. 6.31 Chromatogram showing composition of a synthetic gas mixture when being (A) freshly prepared and (B) two days old.

CHAPTER 7

DEVELOPMENT AND TESTING OF FIELD TECHNIQUES

7.1 Introduction

Since the gas chromatograph is not portable, it was necessary to develop field techniques for obtaining samples of the sulphur gases which could then be transported back to the laboratory for analysis. Furthermore, as the concentrations in soil gas are extremely low, some method of pre-concentration in the field is desirable. Two methods are possible: (a) passive sampling in which an adsorbent is left in the ground over a period of time before being recovered and (b) active sampling in which a relatively large volume of gas is pumped from the soil through an adsorbent which is then returned to the laboratory for analysis. The latter method would have obvious advantage of less delay-time between field sampling and obtaining analytical results. Both approaches were tested at Trefriw and Parys Mountain in the summer of 1976, and active sampling was tested in the following autumn.

Both sampling techniques are critically dependent upon the adsorbent selected. A full and exhaustive investigation into the characteristics of the wide variety of adsorbents available was impossible at this late stage in the project entailing, as it would the probability of many months of laboratory testing. The ideal characteristics for an adsorbent are:

(a) it should strongly and selectively adsorb a wide variety of sulphur gases in very low concentrations from air, at ambient temperatures.

(b) the gases adsorbed should be readily released on heating.

(c) for the passive sampling method the adsorbent must be inexpensive.

(d) the adsorbent must not be irreversible altered at the adsorption temperature so that is may be conditioned at this temperature prior to use.

Two widely differing adsorbents were selcted for initial field trials. These were molecular sieve 13 X and Tenax GC.

Molecular sieve 13 X is a synthetic alkali-metal aluminosilicate similar in many respects to the cubic or robust natural zeolites such as analcite or chabazite. Thus on heating under vacuum water of crystallization is lost leaving a highly porous crystalline structure made up of a framework of the oxides of silica and aluminium. The formula being:

$$0.83 \pm 0.05 \quad Na_2O, Al_2O_3$$
$$2.48 \pm 0.03 \quad SiO_2, nH_2O$$

The structure has a void (internal volume of 51% with an internal surface area of 700 - 800 sq.m/g). The external area is only of the order of 1.3 sq.m/g and hence the major fraction of the adsorption occurs within the internal pores. The molecules that may be adsorbed are therefore limited to those that are physically small enough to enter the pore spaces of the crystal, hence the name molecular sieve. On the basis of advice from M. Hinkle, 13 X was selected from the other alternatives as having a pore diamter large enough to adsrob all the sulphur gases that were likely to be encountered.

Molecular sieves show a strong affinity for water and hence their main use is as drying agents. It is, however, also known that they strongly adsorb the low molecular weight highly polar molecules of hydrogen sulphide and sulphur dioxide as well as the higher molecular weight molecules such as dimethyl sulphide and disulphide. This adsorbent is stable to 700°C.

Tenax G.C. is a porous polymer of 2,6, diphenylpara-phenylene oxide.

The principal use is as a substrate for gas liquid chromatography columns where the properties of a large surface area and high temperature stability have been found to be useful. Recently, however, it has been used as an adsorbent for trace quantities of gaseous contaminants in submarines, space craft and urban atmospheres. The retention of hydrocarbons improves with increasing molecular weight and it is therefore unlikely that the lower molecular weight, inorganic sulphur gases would be retained efficiently.

Passive sampling using molecular sieve proved to be unsatisfactory in the extremely wet conditions of September/October, 1976. However, some indications were obtained by active sampling although these results require a great deal of further research, before they can be considered to be meaningful.

7.2 Passive Sampling

7.2.1 Method

The passive sampling device consists of a 50 ml, 75 mm deep polypropylene jar with a diameter of 48 mm filled with 5 g of conditioned (overnight at 450°C) molecular sieve 13X. The adsorbing molecular sieve was enclosed in the jar with a piece of 125 mesh nylon sheet, which was fastened around the open end of the jar with tape (Fig. 7.1).

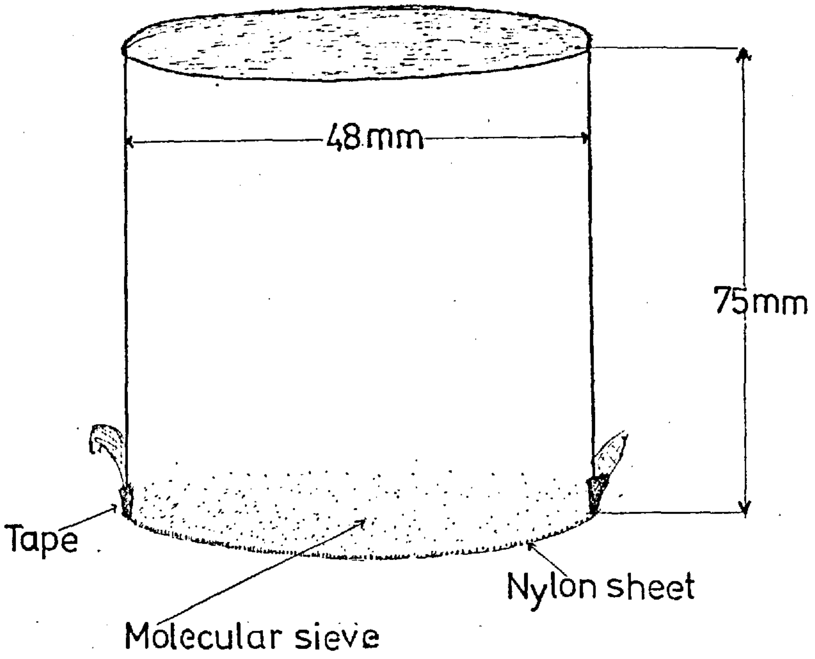

Fig. 7.1 Passive sample jar

The adsorption cup was hung on a steel rod or wooden stick over the bottom of a hole in the soil about 30 - 40 cm deep and 15 cm wide. Fig. 7.2 - 7.3 illustrates the theory of the method and the sampling sites at Trefriw. After sealing the holes with debris and soil, the adsorbents were left undisturbed for about 3 months. At Parys Mountain, the sample sites were selected on basis of the content of visible sulphides in soil and dumps.

By using a long sampling time, the passive sampling technique was considered to eliminate problems of sensitivity, fluctuations in background values and variations due to environmental parameters.

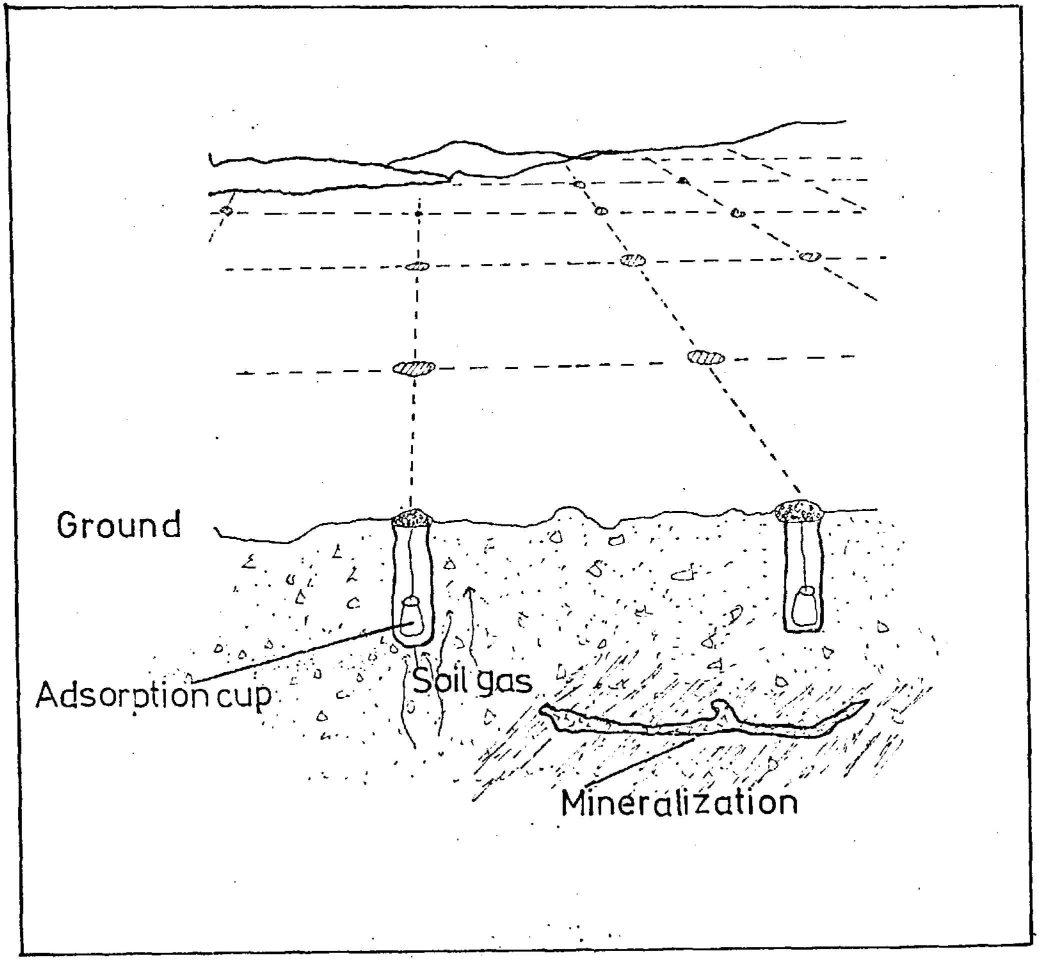

Fig. 7.2 Passive sampling showing adsorption cups placed in a grid system (as suggested in World Mining, March 1976, for measuring radon with the track etch method).

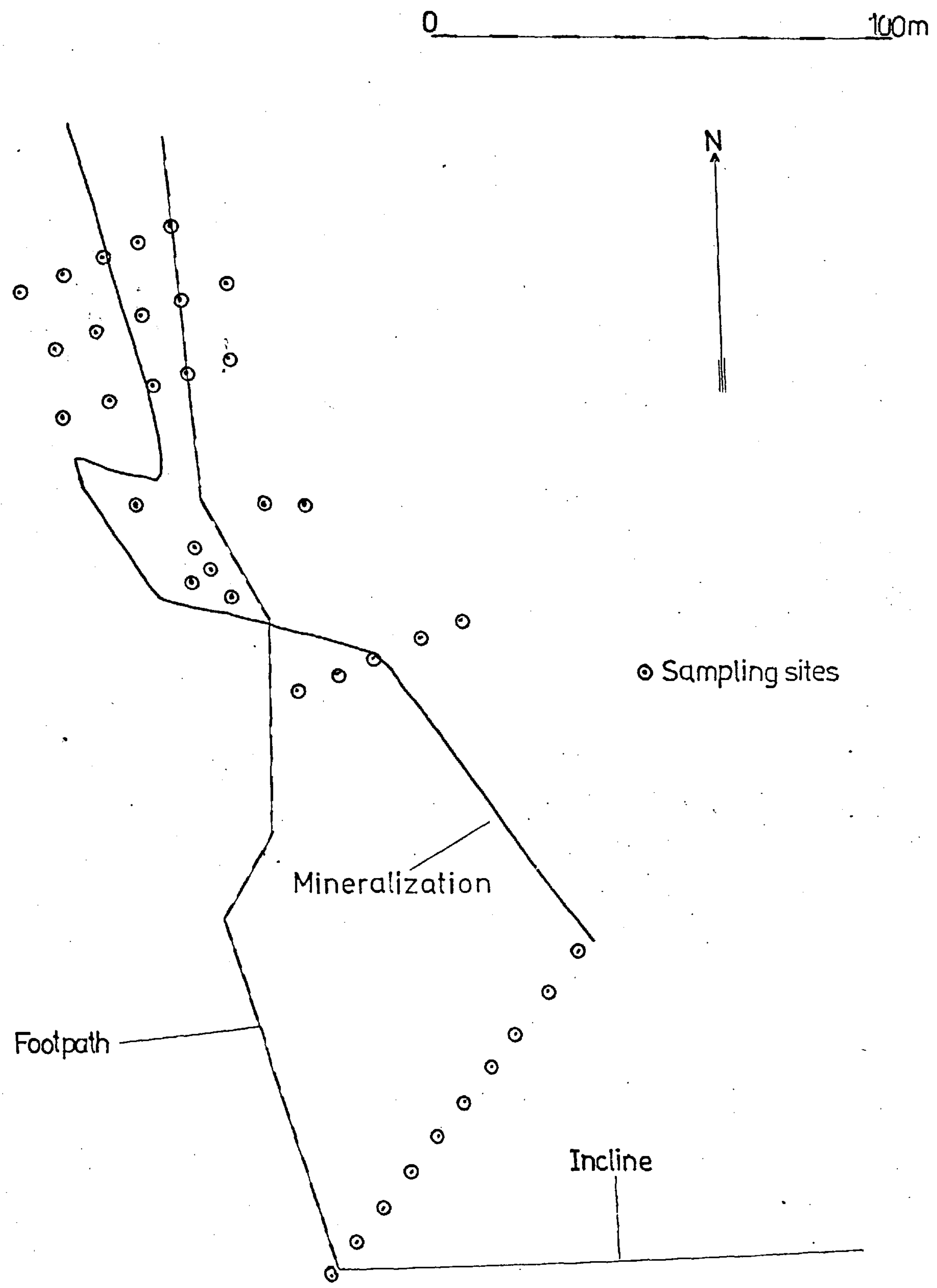

Fig. 7.3 Sites for active and passive samples at Trefriw during July, 1976.

7.2.2 Field Results and Conclusions

After 12 weeks, the passive samples were collected from their sites in Wales. Precipitation and condensation had saturated most samples with water making them useless for analysis and a great number of samples had been destroyed by animals.

Despite the negative results obtained using passive samples in a wet area as Wales, the method might be successfully applied in unconsolidated overburden above oxidizing sulphides in arid and semiarid areas, where precipitation is insignificant. Later work has shown that molecular sieve 13X is not suitable as an adsorbent due to its adsorbing properties for water which is released when the samples are desorbed by heating to 300 - 400°C and cause severe problems when the desorbed vapour is introduced to the chromatograph. Other adsorbents, e.g. Tenax GC (a porous polymer, 2.6 - diphenyl-p-phenylene oxide) are recommended for future tests.

7.3 Active Sampling

7.3.1 Methods

Because of the extremely low concentrations of sulphur gases in the soil atmosphere, it is necessary to concentrate the sulphur volatiles from a large volume of sample. One solution of this problem is to use cartridges containing an appropriate adsorbent through which a large volume of air is drawn. In these active sampling experiments, two adsorbents were tested. Initially molecular sieve 13X was used and latterly also Tenax GC. Fig. 7.4 shows an active sampling cartridge filled with molecular sieve 13X. The method

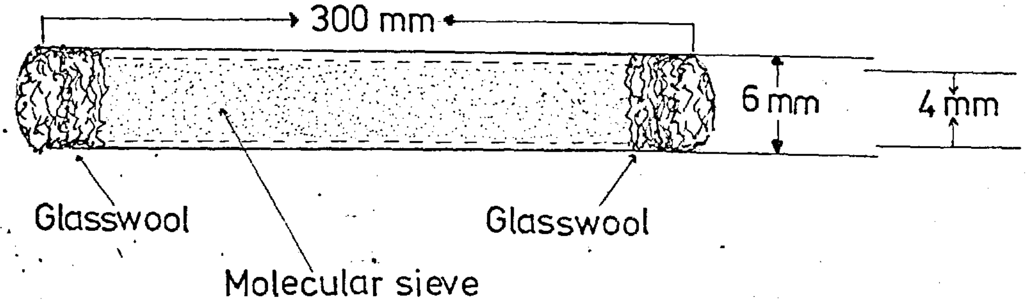

Fig. 7.4 Active sampling tube

entailed the use of a silanized glasstube, 300 mm long with an inner diameter of 4 mm, filled with (1) 1.5 ml conditioned (overnight at 450°C) 85/100 mesh molecular sieve 13X,(2) 1.5 ml, conditioned at 275°C for 30 minutes molecular sieve 13X (85/100 mesh) with argon flushing through the cartridges and (3) 1.5 ml Tenax GC, conditioned for 30 minutes at 275°C under argon flow. Silanized glasswool enclosed the sorbents in the tubes and vinyl caps which, it was hoped, would prevent contamination from the atmosphere. As mentioned elsewhere, fieldwork was carried out during the summer and autumn seasons. Different sampling and analytical techniques were used. The critical phase using this sampling technique is the analysis; of the samples. Only trace quantities of sulphur gases are adsorbed in the cartridges and it is important that the entire sample should be submitted to the chromatograph for analysis. The trapped gases were thermally desorbed and finally brought to the column with argon carrier gas. A detailed description of the analysis of the cartridges is given below.

7.3.1.1 Sampling

In the collection of sulphur gases the following items were employed. A Teflon tube (inner diameter 3 mm) was led into the hollow stem of a stainless steel auger used for gas sampling.. All contact between the metal surface of the auger and the sulphur volatiles was thus avoided. A 3 - 4 cm long Teflon tube (inner diameter 4 mm) connected the outlet of the auger to the adsorption tube. The sample was drawn through the adsorbent with the aid of a 100 ml Gastec hand pump or a Capex Mark 2 suction pump, powered with a car battery. The flow-rate was controlled with the aid of an adjustable flow-meter, when the Capex Mark 2 pump was used. Fig. 7.5 illustrates the sampling apparatus.

After driving the auger in the soil, the holes near the tip were cleaned by blowing air into the Teflon tube with the aid of a hand rubber bellow. At Trefriw, sample sites were chosen as indicated on Fig. 7.3 and Fig. 7.6. In the screening procedure, dumps, soil and the free atmosphere were sampled for sulphur gases. At Parys Mountain, dumps and sites with visible sulphides were selected as suitable sampling sites. In the summer fieldwork, an intense odour of oxidizing sulphides could be recognized in both areas, while in the autumn season the odour was most intense at the Trefriw main adit. In the initial tests, using the active sampling method,

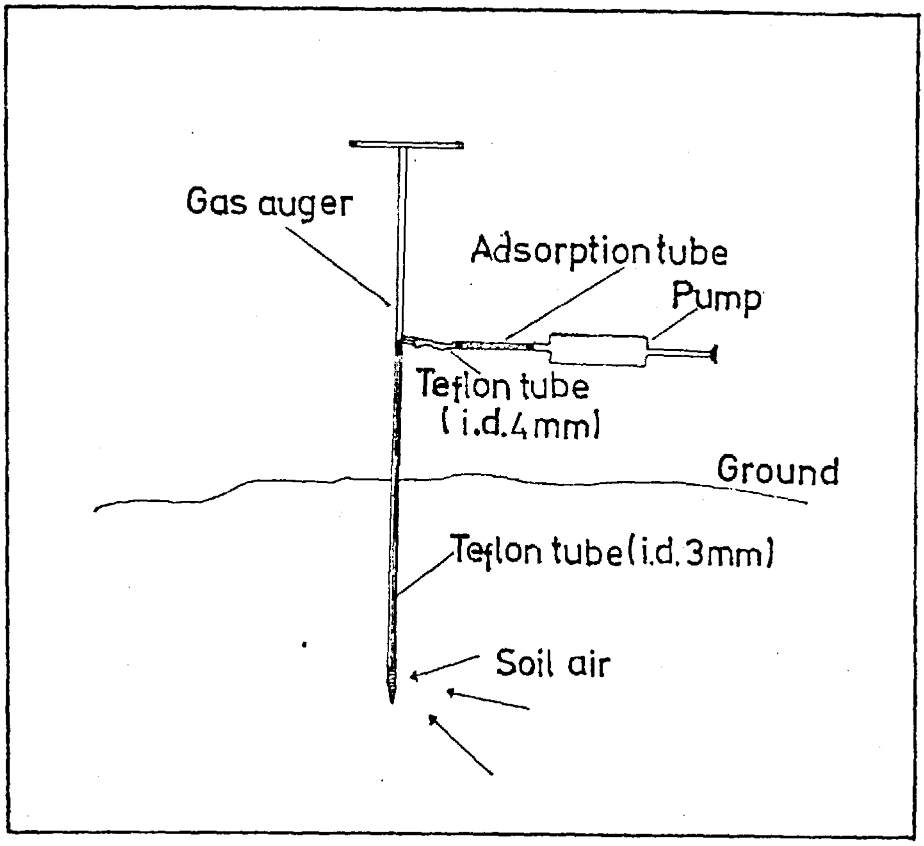

Fig. 7.5 Sulphur vapour adsorption apparatus for sampling soil gas

molecular sieve 13X (conditioned at 450^{o}C overnight) was used and 1 ℓ air was sampled and drawn into the adsorbent with the aid of the Gastec hand-pump. At each site, three samples of the same volume were taken. In the autumn, cartridges packed with either molecular sieve 13X or Tenax GC were used, through which a sample volume of 5 - 15 ℓ was drawn with the aid of the Capex Mark 2 suction pump using a flow-rate of 0.5 ℓ/min. After sampling, the adsorption tubes were stored in glass containers to avoid post-sampling contamination. (Soil samples were collected at each sample site and were stored in either dark or transparent 50 ml Sovirel glass

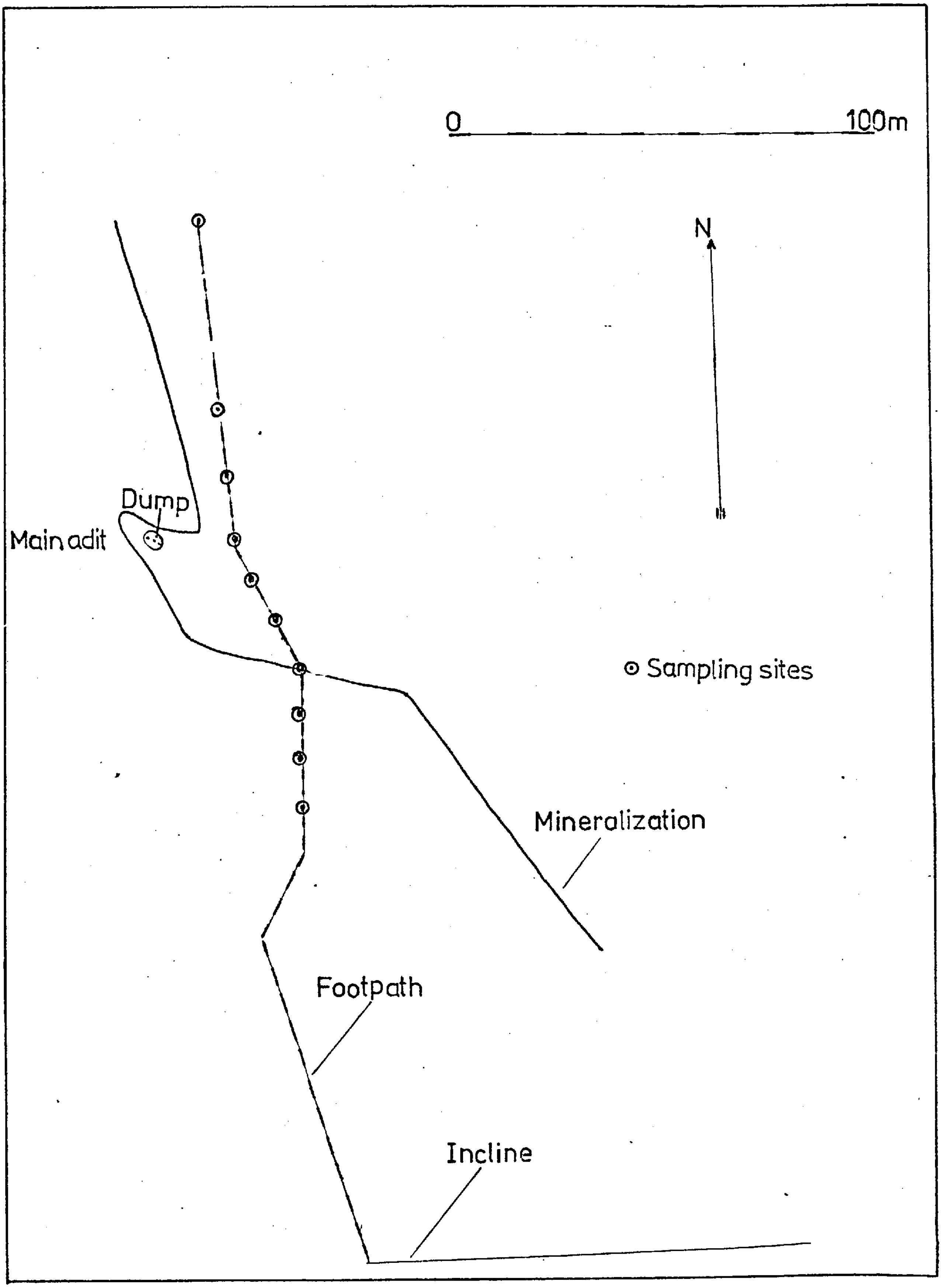

Fig. 7.6 Sites for active sampling at Trefriw during Nov., 1976.

bottles which were put into boxes filled with either solid carbon dioxide or ice with the objective of eliminating post-sampling microbial reactions in the samples).

7.3.1.2 Desorption

In the analysis of the trapped sulphur gases, the sample cartridges were heated to 300 - 350°C and the thermally liberated sulphur volatiles were transferred to the column with argon carrier gas. Two different types of desorption systems were used. The first entailed the use of a sample loop, in which the sulphur gases were collected before presentation to the column and the second method employed a cool-trap, in which the sulphur volatiles were pre-concentrated before being transferred to the separating column. Both methods are described below.

The thermal desorption system used in the analysis of the molecular sieve 13X-filled sample cartridges, which were used during the summer fieldwork is depicted in Fig. 7.7. The system consists of basically three main components; a 32 cm long rectangular insulated desorption chamber of brass which is heated to 350°C by two washing-boiler elements; a Teflon Omnifit 3-way valve, providing the switching unit needed to evacuate and fill the third main component, which was a six-port Perkin-Elmer stainless steel precision valve equipped with a 0.1 ml stainless steel sample loop. In attempts to avoid a too rapid temperature decrease between the desorption chamber and the two valves, the latter and the ⅛-inch Teflon tube connections between the different components

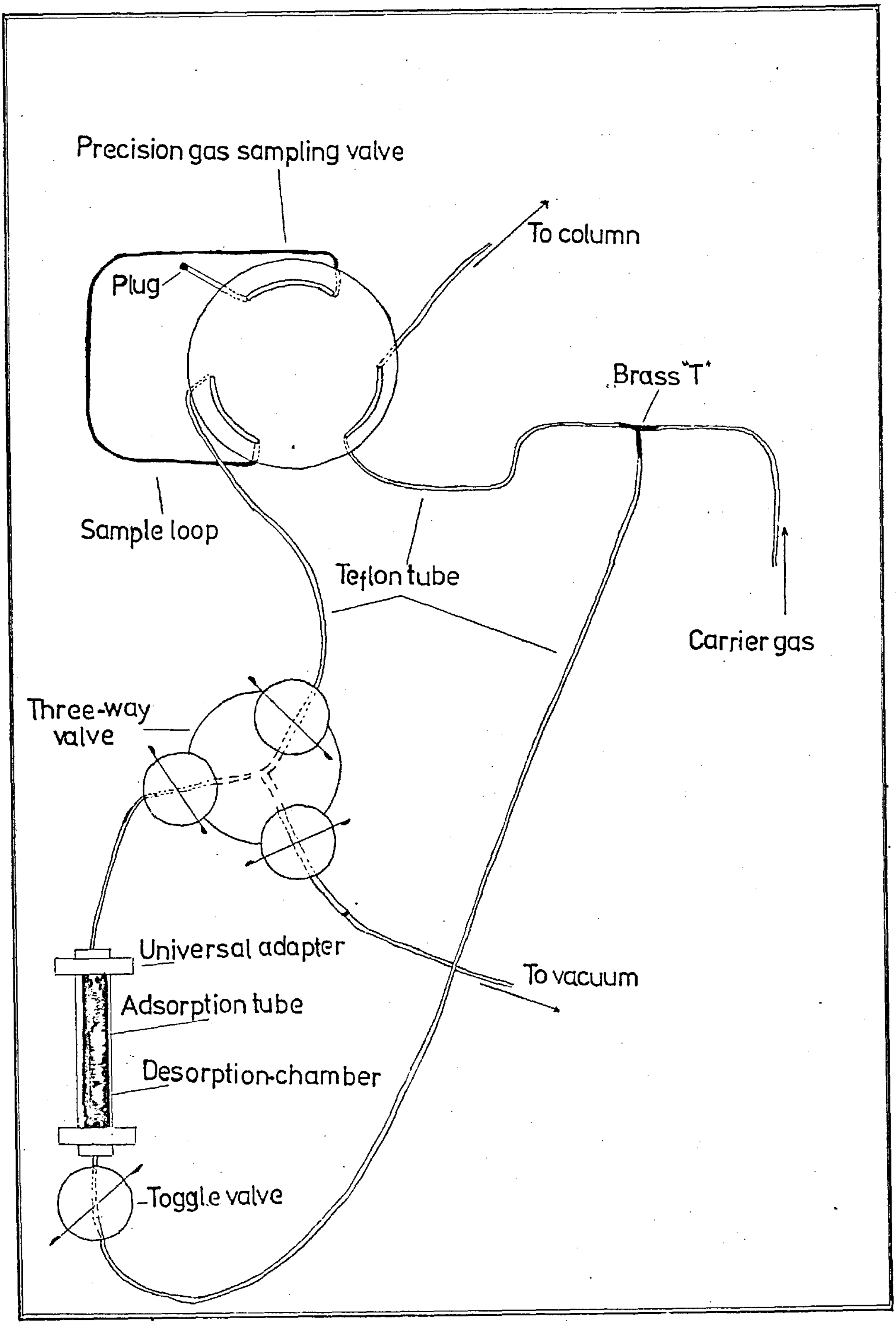

Fig. 7.7 Thermal desorption system for adsorption tubes.

were encased in an asbestos box which was heated by a 60w light bulb. The desorption chamber temperature was controlled and monitored with a Gallenkamp temperature controller and a Variac transformer. The former comprises two components, a temperature sensor and a control box, which are linked together by a capillary tube. The working procedure is summarized below.

(1) The adsorption tube was connected to the carrier gas supply and the Omnifit valve and heated to 350°C in the desorption chamber for 3 minutes, with the argon carrier gas switched off.

(2) The sample loop was evacuated in the meantime.

(3) After 3 minutes, the carrier gas was turned on for 1 minute and the liberated sulphur gases were transferred to the 0.1 ml sample loop.

(4) Thereafter, the sulphur gases were presented to the chromatographic column.

(5) Finally, the carrier gas was turned off with the aid of a toggle valve (see Fig. 7.7) and the precision gas sampling valve was closed.

The results of the analysis using this method are presented below. It is necessary to mention that sulphur gases were detected in both sample tubes and blanks. In attempts to clean the system and to avoid "memory" effects from sample to sample, all stainless steel tubes in the precision gas sampling valve were replaced with $^1/_{16}$-inch Teflon tubes. Subsequent experiments showed no improvement and further work on this aspect of the technique was consequently discontinued. A new desorption technique described below, was finally designed.

The analytical desorption-gas chromatographic system is illustrated in Fig. 7.8 and consists mainly of two components; a desorption heater, heated by a Nichrome wire element, directly connected to the gas chromatographic

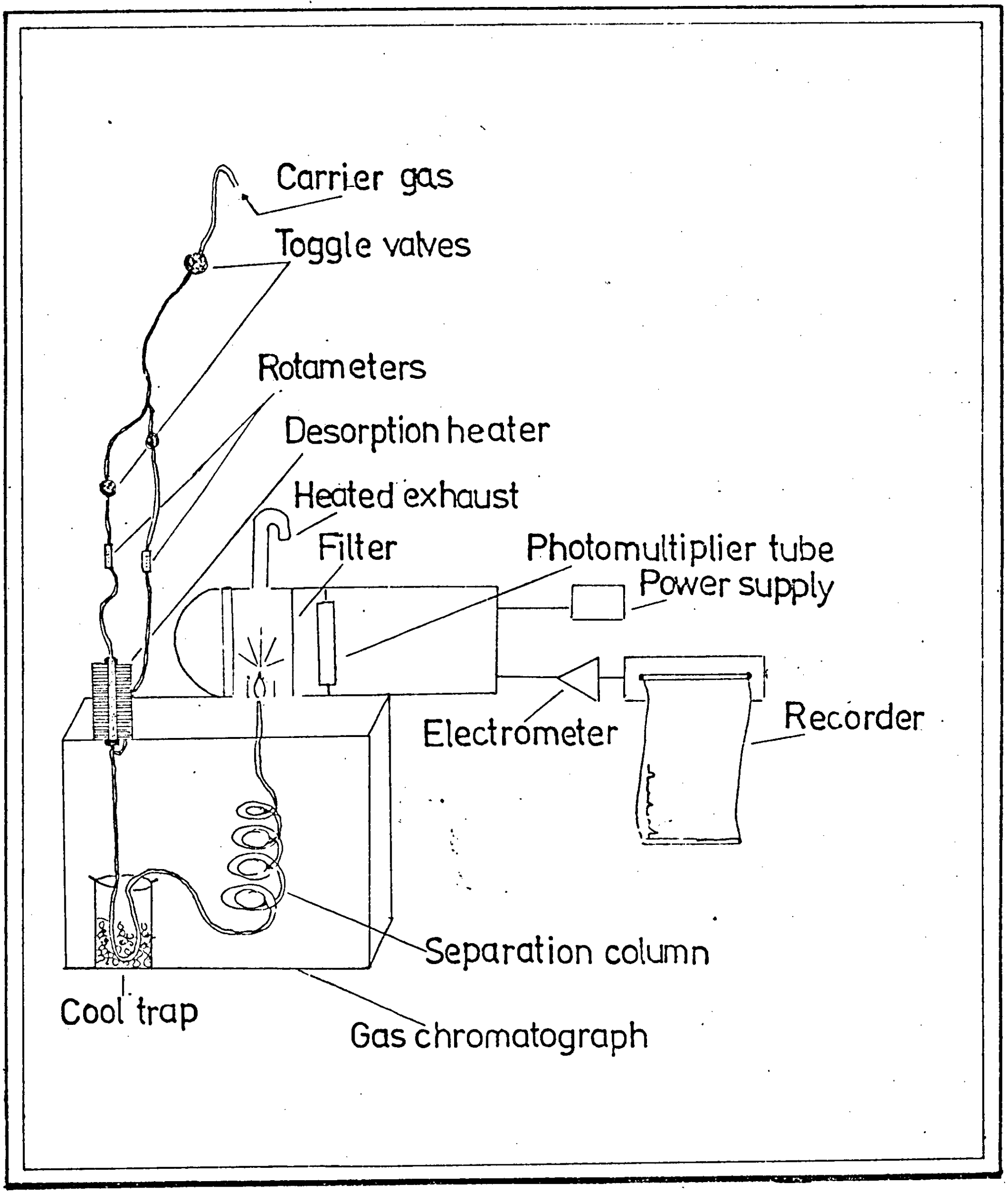

Fig. 7.8 Gas chromatographic system showing the desorption chamber and the cool-trap for liberated sulphur gases.

injection port, and a cool trap, consisting of an 8 cm long pre-column which is cooled in a mixture of solid carbon dioxide and isopropanol, giving a temperature of -80^{o}C. The cool trap condenses the sulphur gases as liquids in a small carrier gas volume before being analysed. Acceptable chromatographic performance is impossible unless gases are presented in concentrated form as compared with continuous stripping of the gases from the sorbent. Toggle valves were used to provide switching facilities for the carrier gas. The temperature was maintined at 300 - 350^{o}C controlled by a Variac transformer and a Gallenkamp temperature controller.

The adsorption cartridge was placed in the pre-heated desorption heater for 3 minutes with the carrier gas switched off. The pre-column was at the same time immersed in the freezing mixture of solid carbon dioxide and isopropyl alcohol. Thereafter, the carrier gas was turned on and the liberated sulphur gases were transferred to the cooled pre-column, where they were concentrated for 1 minute before analysis. Thereafter, the carried gas was switched off, the cool-trap removed and the column oven door closed. After another 2 minutes, when the oven temperature was 50^{o}C, the carrier gas was turned on and the released pre-concentrated sulphur gases were swept to the separation column. Using this technique, about two samples/hour were analysed using the temperature programming presented in Table 6.3

7.3.1.3 Results of sampling at Trefriw and Parys Mountain

The objectives of the experiments at Trefriw during the summer and autumn of 1976 were twofold. The main aim was to test techniques, methods and adsorbents in a field situation to determine whether it was possible to collect sulphur gases and return them to the laboratory for analysis. The second and minor objective was to try to collect sulphur gases from soils overlying sulphide mineralization.

The experiments have proved to be an essential, although unfortunately not final, stage in the development of a optimum field method. The techniques used during the active sampling in the summer demonstrated the shortcomings of the desorption method which concealed the problems arising from adsorbed water and contamination of the packing which were only revealed after the autumn sampling. The principal areas of error in the earlier technique were considered to be:-

(a) 'memory' effects from sample to sample and from sample to blank which were ascribed to reversible adsorption of sulphur gases on to the tubes and valves of the desorption and transfer equipment

(b) the small fraction of the desorbed gases that was actually transferred to the column for analysis.

(c) contamination of the adsorbent due to conditions prior to filling the cartridges.

The effects of the desorbed water were concealed by the fact that the actual volume of water put on to the column was small and, more importantly, the water vapour was not allowed to condense.

Following the modifications to the equipment and techniques described above, a number of other difficulties were revealed. The most serious of these has arisen from contamination of the adsorbents during storage. The tubes were conditioned prior to use by purging with argon at 275°C for 30 minutes. Testing immediately after conditioning proved that the tubes were clean enough to be acceptable. It was extremely difficult to achieve absolute cleanliness and true blanks. The contamination arose during storage and transport to and from the field area. The severity of the difficulties is shown in Figs. 7.9 - 7.11 which are, respectively, chromatograms derived from a blank glass tube, and two tubes packed with molecular sieve unused and after passing 1 litre of soil air from over the mineralization at Trefriw. It is readily apparent that there are high levels of contamination in the unused tube and that the differences between the sample and the blank are insignificant. Furthermore desorbed water that has condensed and collected on the column during desorption has passed into the vapour state at 100°C generating a meaningless collection of peaks. The chromatograms shown in Figs. 7.12 and 7.13 are further illustrations of the effects of water vapour on the analysis. They are derived from the gases desorbed from molecular sieve cartridges after the passage of 5ℓ and 15ℓ of the sulphur gas -rich atmosphere in the main adit at Trefriw.

From this it can be concluded that, with this system of desorption and presentation to the chromatograph, molecular sieve, or any other adsorbent that collects water-vapour is unsatisfactory. It is also plain that the method of storing the tubes must be improved to prevent contamination.

The samples collected using Tenax GC are subject to the same doubts as those using molecular sieve as the storage method was identical in both cases. However Tenax does not adsorb water and the chromatograms are therefore somewhat more acceptable.

The initial analyses of the blanks and used sample tubes appeared to show some promise. Fig.7.14 shows the analysis of the gases derived from a blank (unused) Tenax tube. There are only three peaks, of which the major one appears to be sulphur dioxide. However this must be viewed with some doubt as Tenax would not be expected to efficiently trap sulphur dioxide and it is possible that the gas has been formed as a result of heating the adsorbent in the presence of the atmospheric oxygen retained within the tube. The chromatograms illustrated in Figs. 7.15 and 7.16 are derived from used sample tubes through which 5 and 15ℓ of adit air had been passed. There are a number of sulphur gas peaks and the larger sample seems to show greater amounts espeically of the later organic sulphur gases which would logically be expected to be preferentially adsorbed onto Tenax. Sulphur dioxide appears to be present as a major component of the gas mixture, a result that is not in agreement with our previous experience. There are a number of possible explanations for this:

(i) The sample is a true representation of the composition of the gas mixture and this method is superior in detecting sulphur dioxide.

(ii) The gas is an artifact produced during the heating of the adsorbent with its adsorbed sulphur gases in the presence of oxygen prior to concentration on the column.

(iii) The sulphur dioxide is derived from contamination of the adsorbent during transport and storage.

A duplicate suite of sample tubes were despatched to the laboratories of Unilever who had kindly offered to analyse the gases desorbed from the adsorbents on a GC/Mass spectrometer system. They reported that they were unable to detect any gases on the used sample tubes that were not present in the blanks.

Attempts to repeat the results of the adit atmosphere sampling during the spring of 1977 but with the tubes being stored before and after use in sealed glass ampoules have also not met with success. Sulphur gases, where present, were only detected in minor quantities.

It is therefore felt that the most likely explanation of the chromatograms is a combination of (ii) and (iii) above. However, it is suggested that, although not confirmed, the results are of sufficient interest to justify further attempts to repeat them under more rigourous experimental conditions.

In view of the doubtful nature of the results of sampling the sulphur-rich atmosphere of the adit, it is felt that presentation of the results of sampling soil air at Trefriw and Parys Mountain would not be valid at this stage.

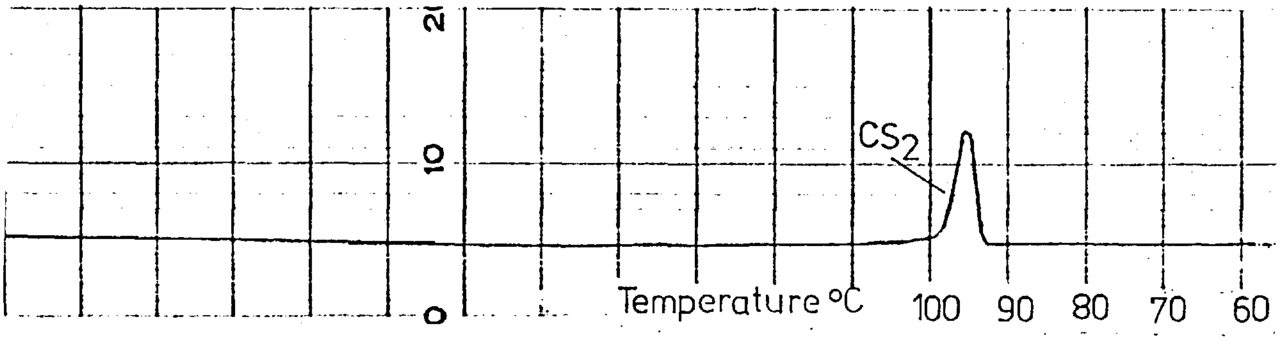

Figure 7.9 Chromatogram showing carbon disulphide liberated from a glass tube (the carbon disulphide is derived from the carrier gas stream and has been concentrated by the cold trap).

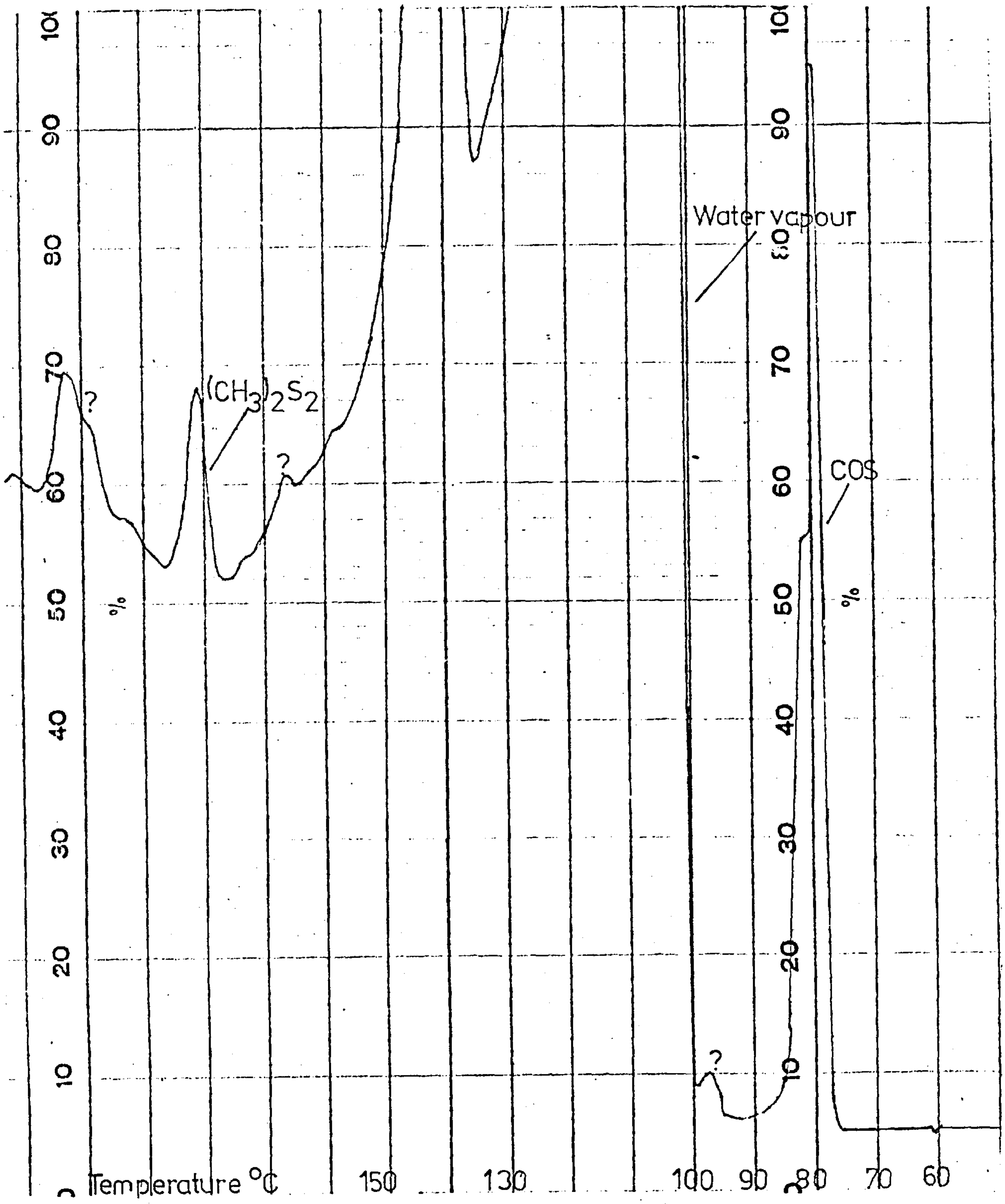

Fig. 7.10 Chromatogram showing sulphur gases liberated from blank molecular sieve 13X.

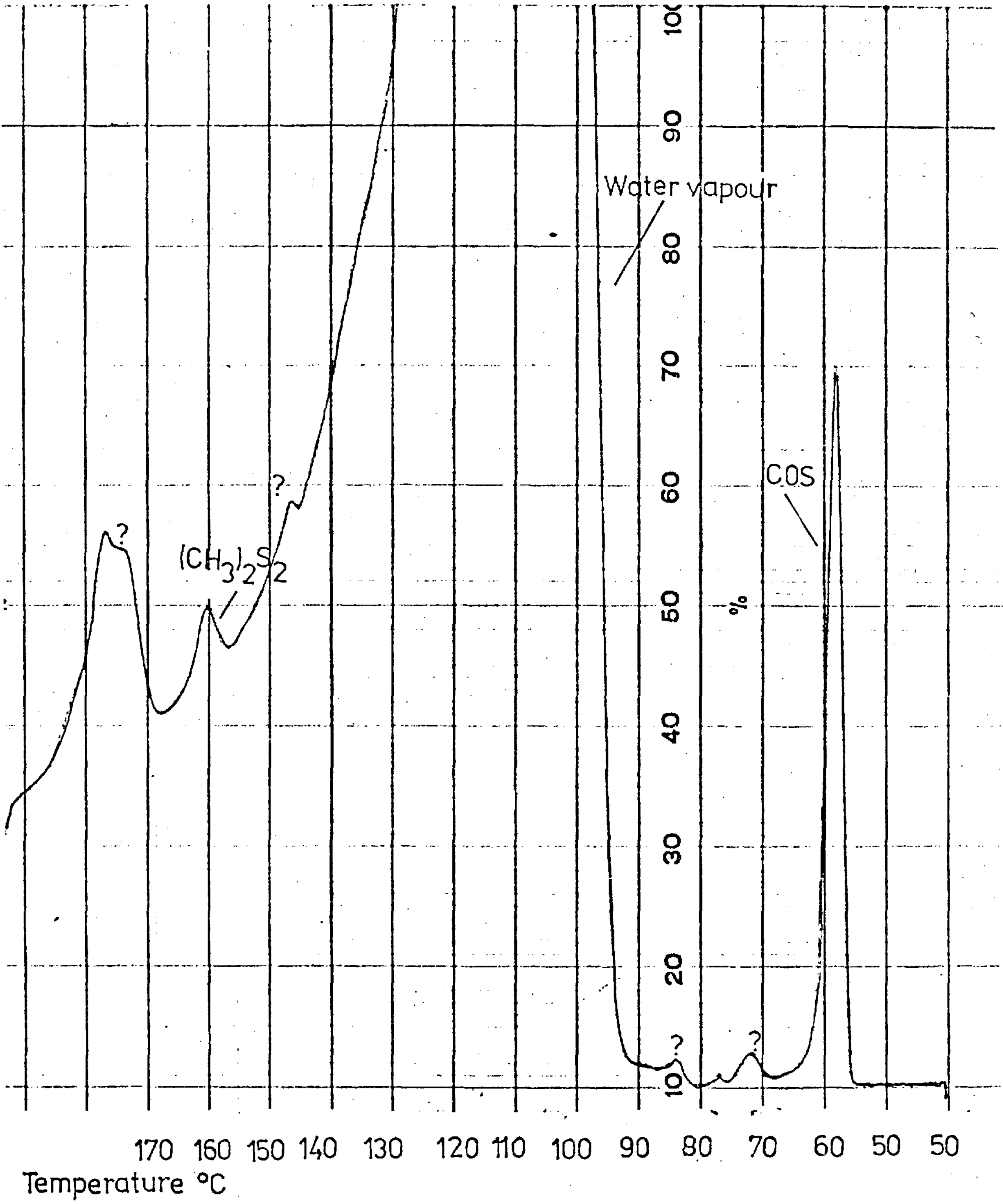

Fig. 7.11 Chromatogram shwoing sulphur gases liberated from a 1 ℓ soil air sample from Trefriw adsorbed on molecular sieve 13X.

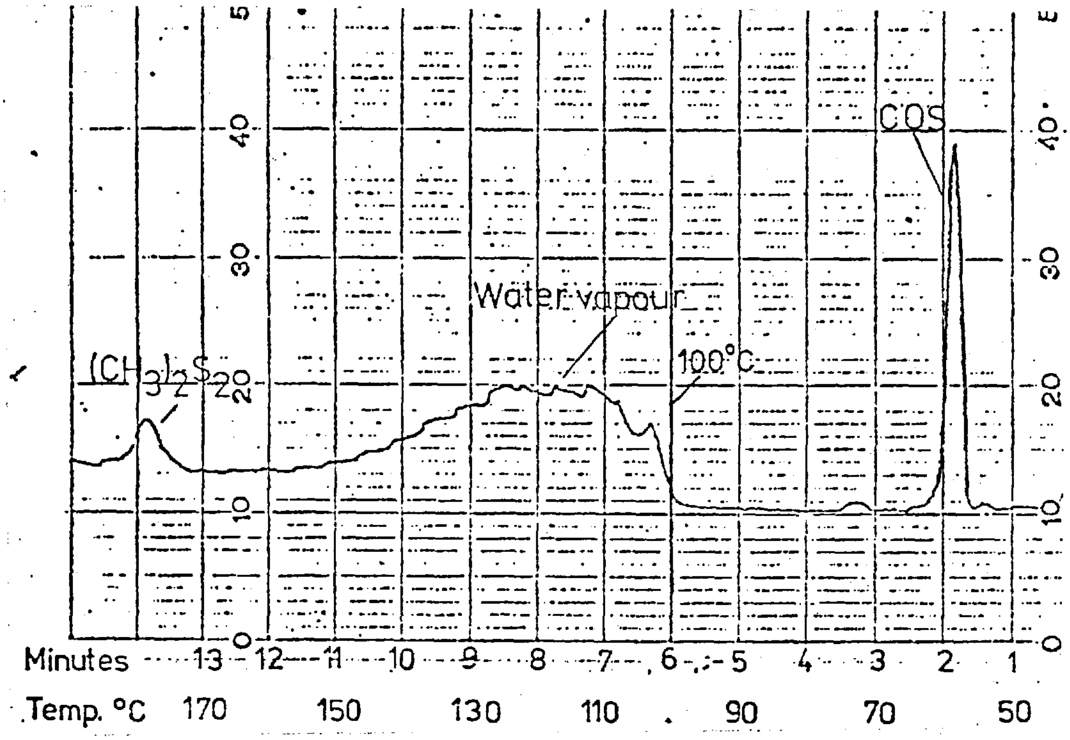

Fig. 7.12 Analysis of 5 ℓ of atmosphere from the main adit at the Trefriw pyrite deposit adsorbed on molecular sieve 13 x. The chromatogram shows the elution of water, starting at 100^{o}C.

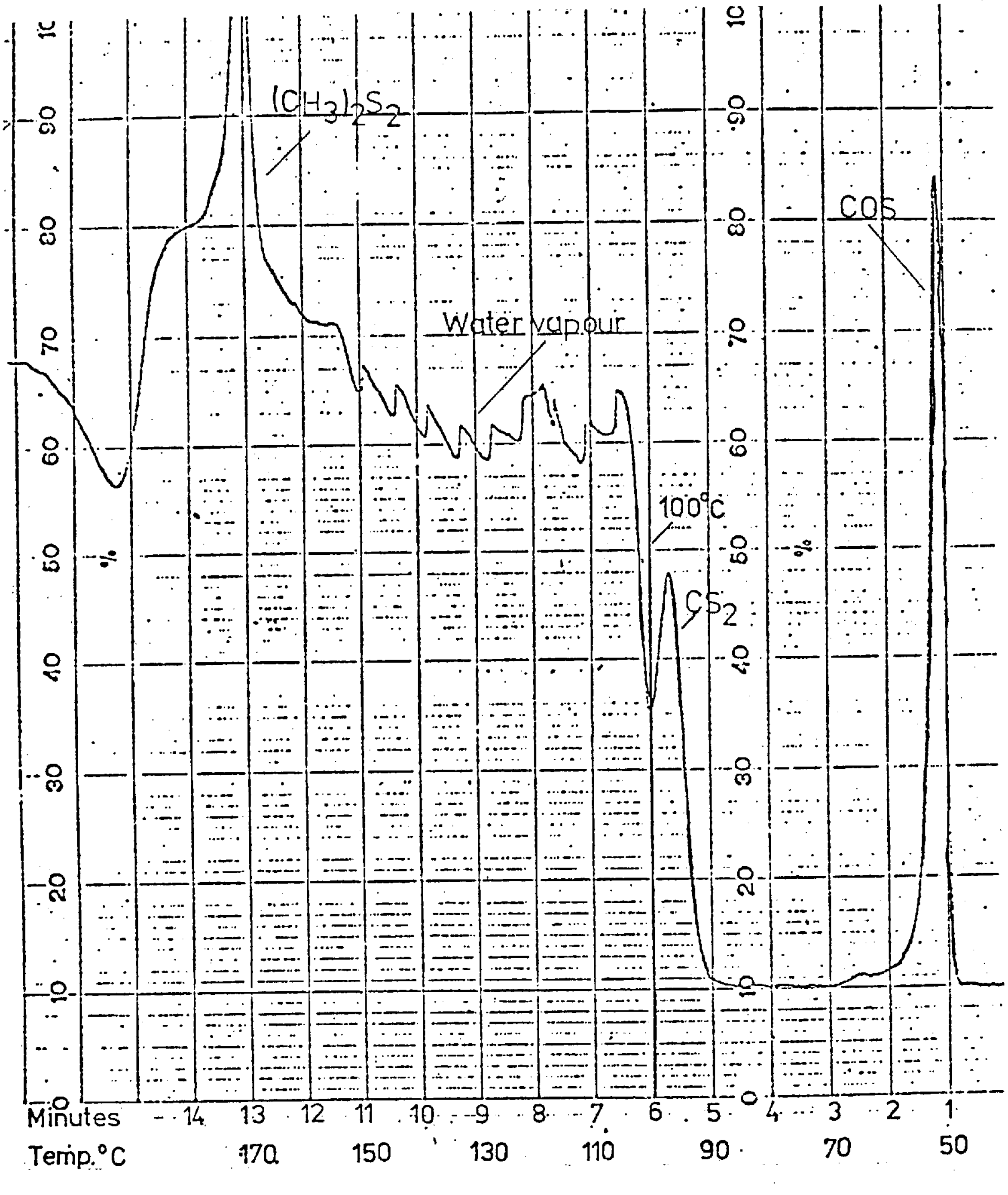

Fig. 7.13 Analysis of 15 ℓ sample of atmosphere from the main adit of the Trefriw pyrite deposit, adsorbed on molecular sieve 13X. The chromatogram shows the elution of wate starting at 100°C.

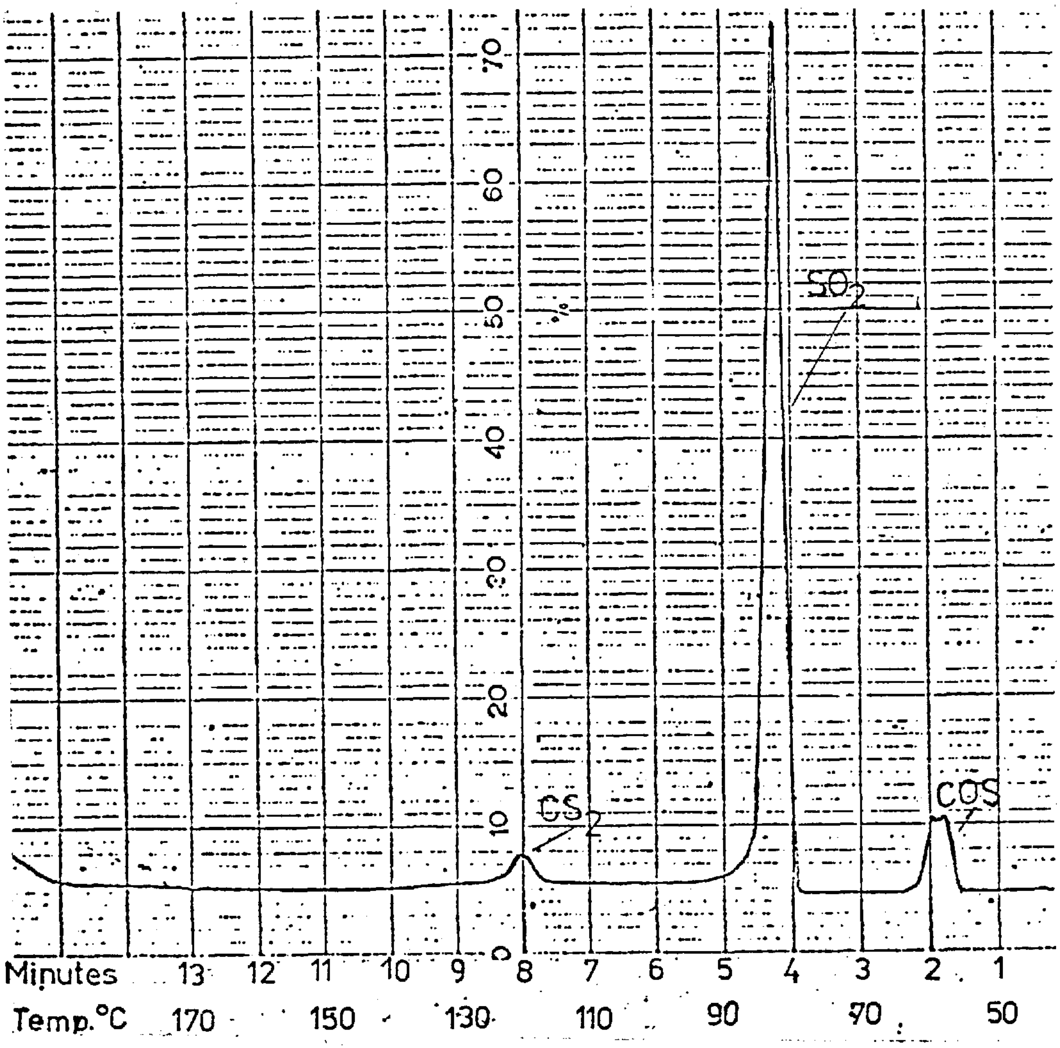

Fig. 7.14 Chromatogram showing volatile sulphur compounds liberated from blank Tenax GC.

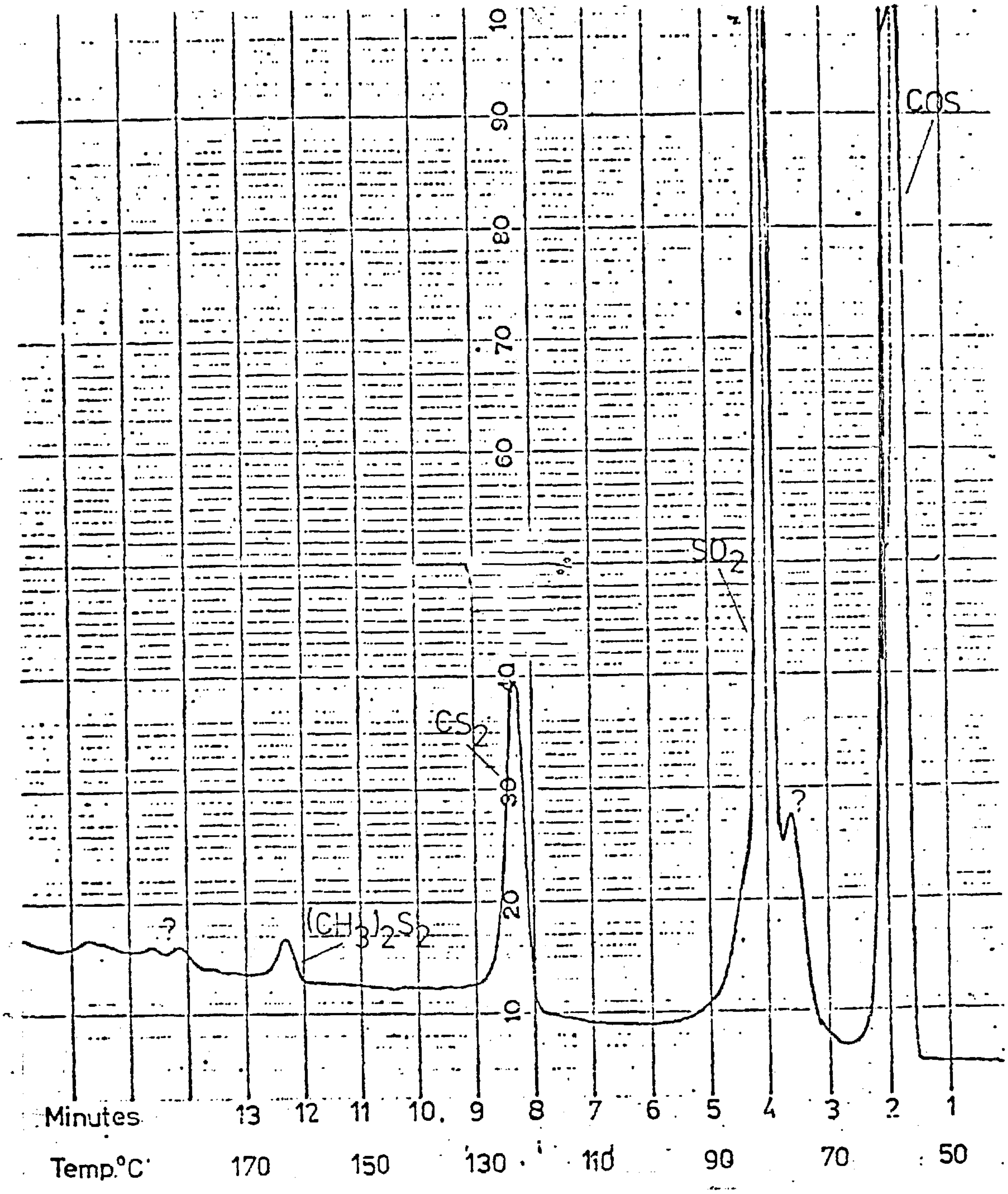

Fig. 7.15 Chromatogram showing the analysis of a 5 ℓ sample of atmosphere from Trefriw main adit adsorbed on Tenax GC.

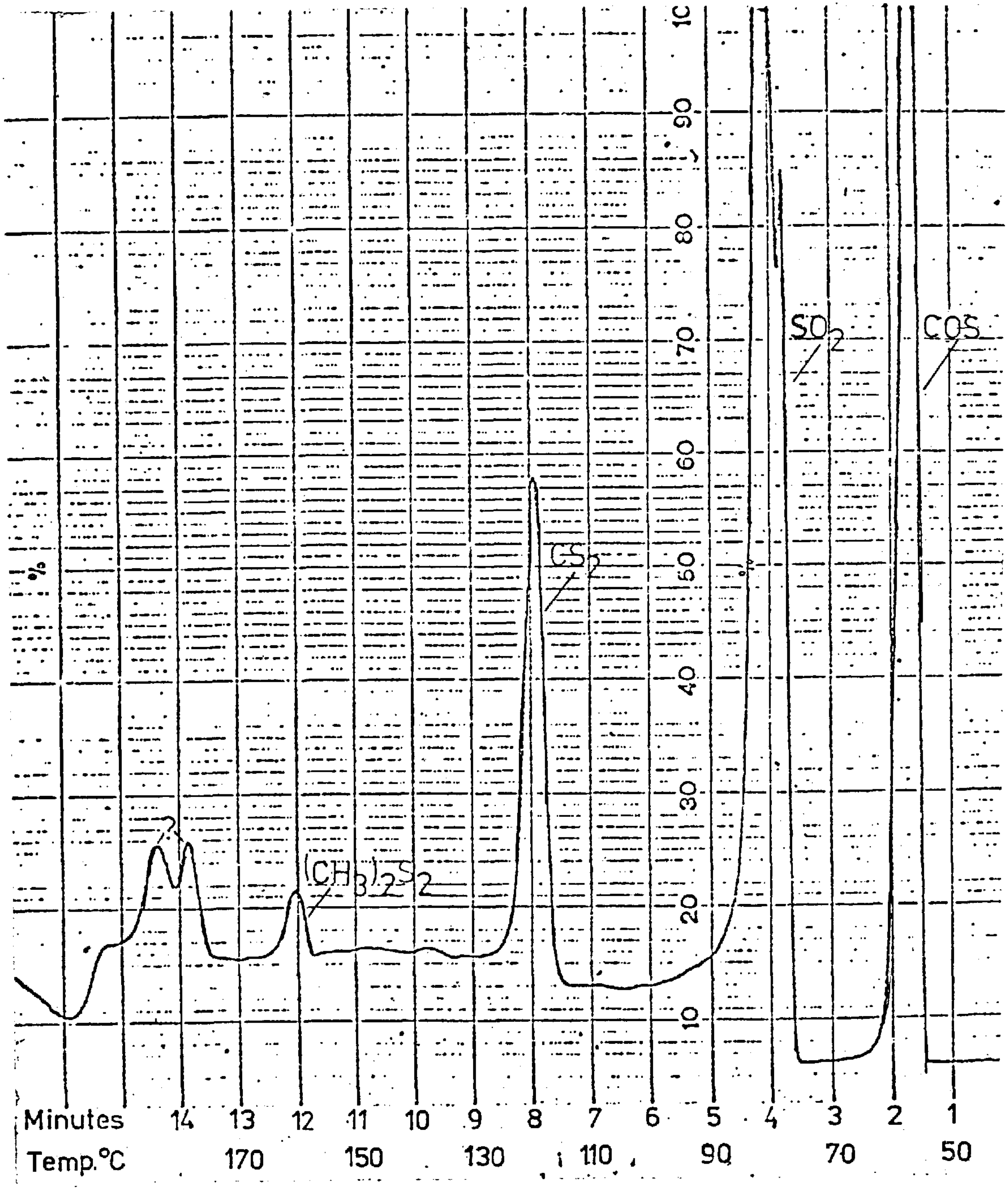

Fig. 7.16 Chromatogram showing the analysis of 15 ℓ of atmosphere from Trefriw main adit adsorbed on Tenax GC.

When it became clear that the results of the soil gas sampling were doubtful other alternative methods of investigating soil gas were considered. The most attractive alternative appeared to be the use of the soils themselves as natural adsorbents. It was hoped that the soils would act as a passive sampler of the sulphur gas flux between the atmosphere and buried sulphides. The "integration" period could be considered to have been sufficient to have permitted equilibrium conditions to be achieved. Unfortunately the soils collected at each sample site for "backup" conventional geochemistry had been dried and were therefore unsuitable. Soil samples that had been collected as part of another experiment, which is described below were taken and placed in sealed septum bottles. After incubation for seven days, samples of the headspace gas were removed by syringe and injected onto the gas chromatograph for analysis.

It became clear that the headspace gas from soils that had been collected near the mineralization at Trefriw (Fig. 7.17 and 7.18) released appreciable quantities of carbonyl sulphide and carbon disulphide whereas those over soils collected away from the mineralization,of which Fig. 7.19 is typical, did not. The sensitivity setting of the machine is the same for all three chromatograms.

These results, are of considerable interest, but will require confirmation.

A further experiment was undertaken to investigate the importance of microbiological activity in the evolution of sulphur gases from oxidizing sulphides. Samples of fresh and weathered sulphides were collected as were a number of soils from both background and mineralized areas at Trefriw and Parys Mountain. Samples were collected in duplicate and some sterilized by a heavy dosage of gamma radiation at Harwell Atomic Energy Establishment.

Prior to irradiation the samples were kept at a low level of biological activity by cooling. The samples to be sterilized being cooled in solid carbon dioxide and the non-sterile set were stored in ice. After sterilization both sets of sample bottles were incubated at 30°C for three days before being tested by headspace gas analysis. The analyses were repeated at three day intervals for two weeks.

No clear trends were established although non-sterile samples tended to have lower levels of sulphur gases than those that had been rendered sterile. Figs. 7.20 and 7.21 are typical of the results obtained. A possible explanation of this result is the release of adsorbed sulphur gases (especially carbonyl suphide) as a result of heating during the irradation. However, the experiment must be repeated under more rigourous conditions, perhaps using artificially generated sulphides, before the results can be clarified.

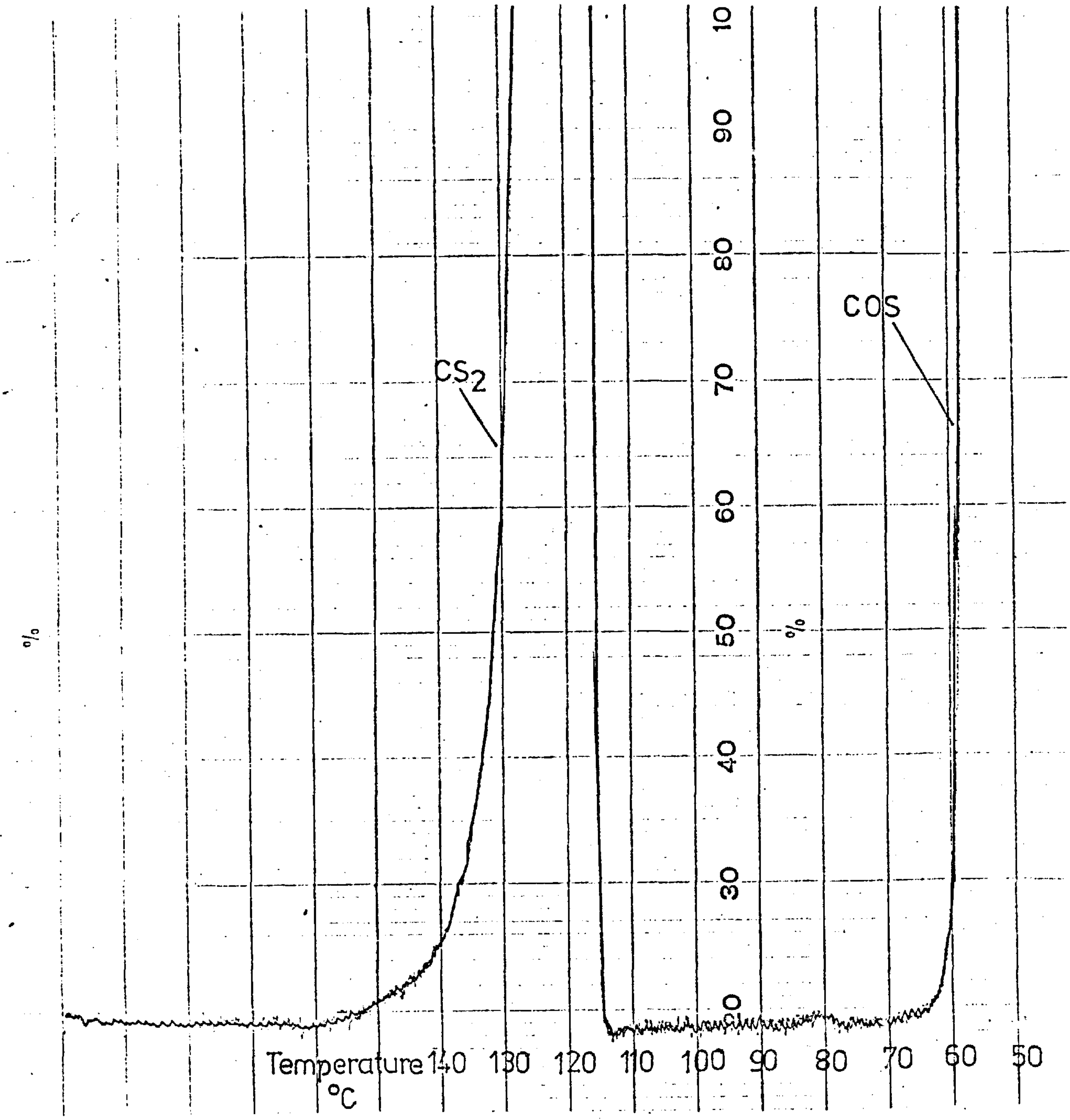

Fig. 7.17 Chromatogram showing composition of headspace gas over soil near mineralization at Trefriw.

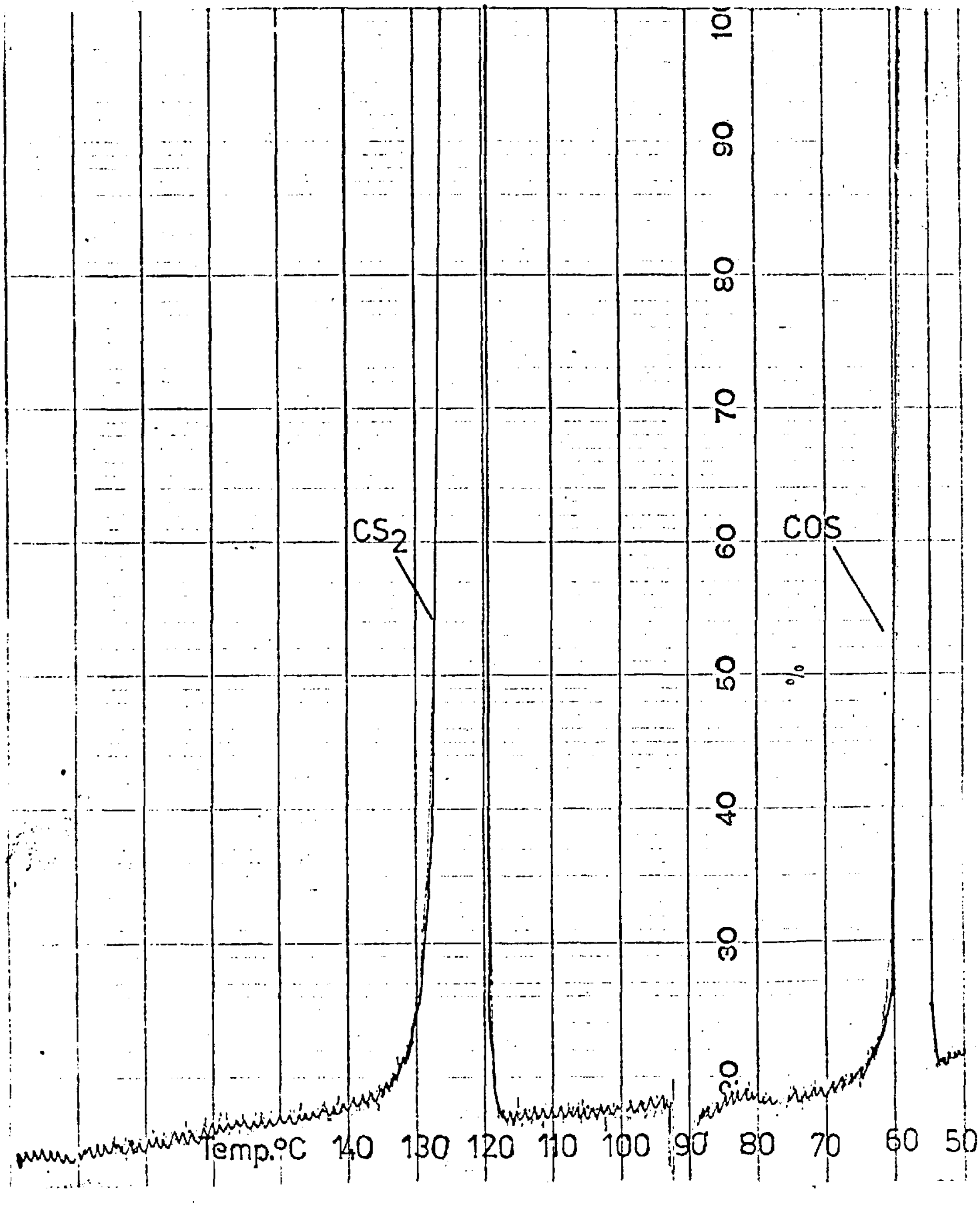

Fig. 7.18 Chromatogram showing composition of head-space gas over soil near mineralization at Trefriw.

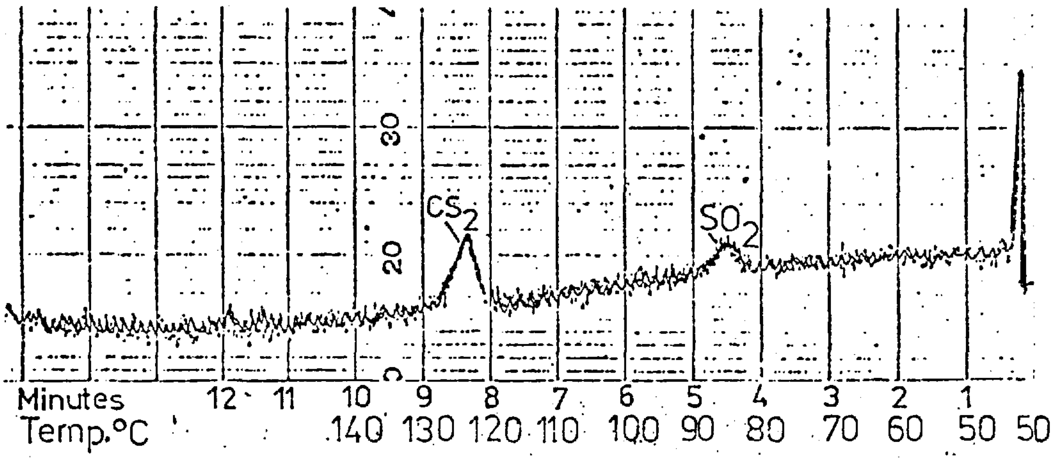

Fig. 7.19 Headspace gas analysis of soil 50 m from mineralization at Trefriw

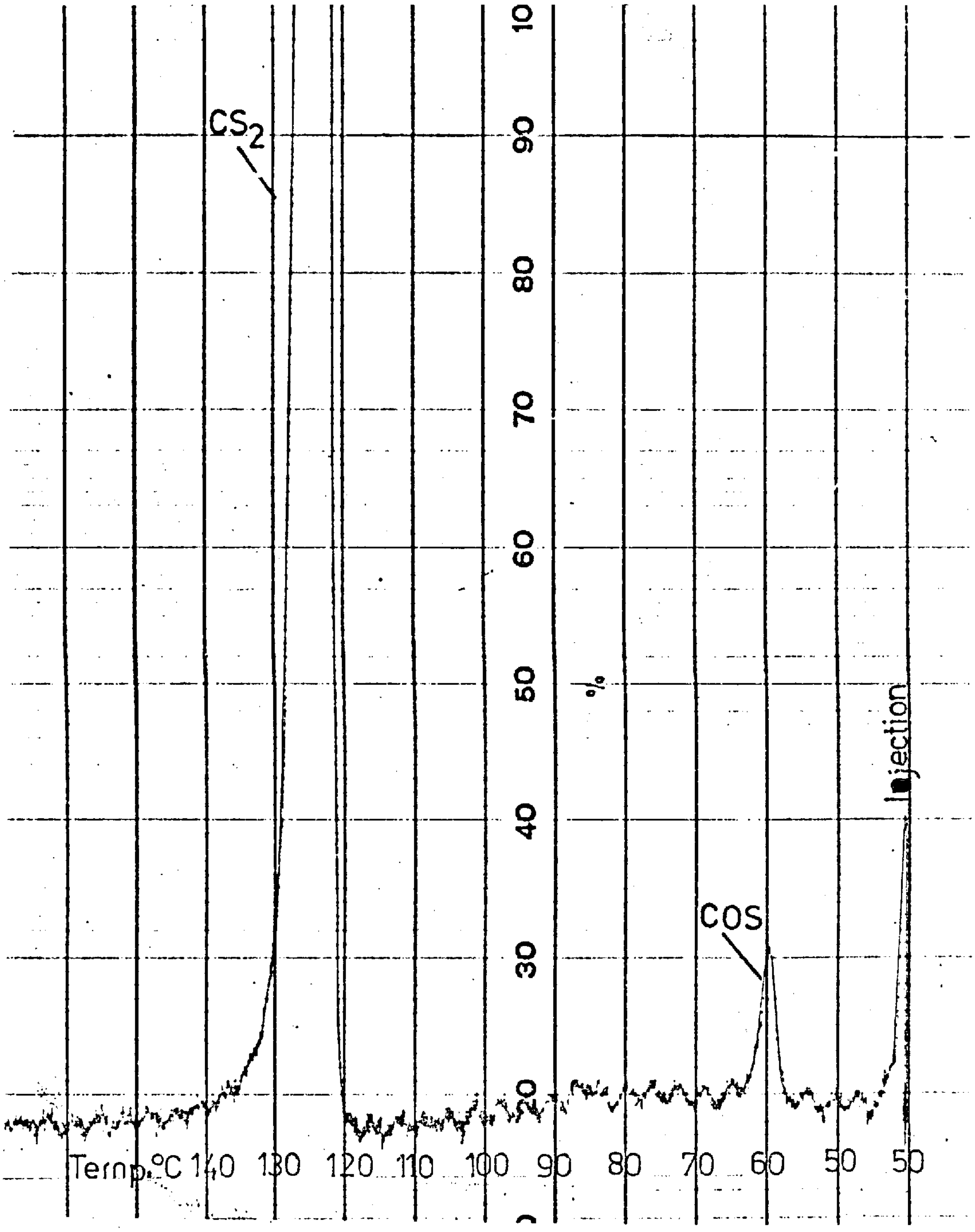

Fig. 7.20 Chromatogram showing presence of carbonyl sulphide and carbon disulphide in the head-space gas over a non-sterile sample of a Trefriw dump near the entrance of the main adit (after six days incubation).

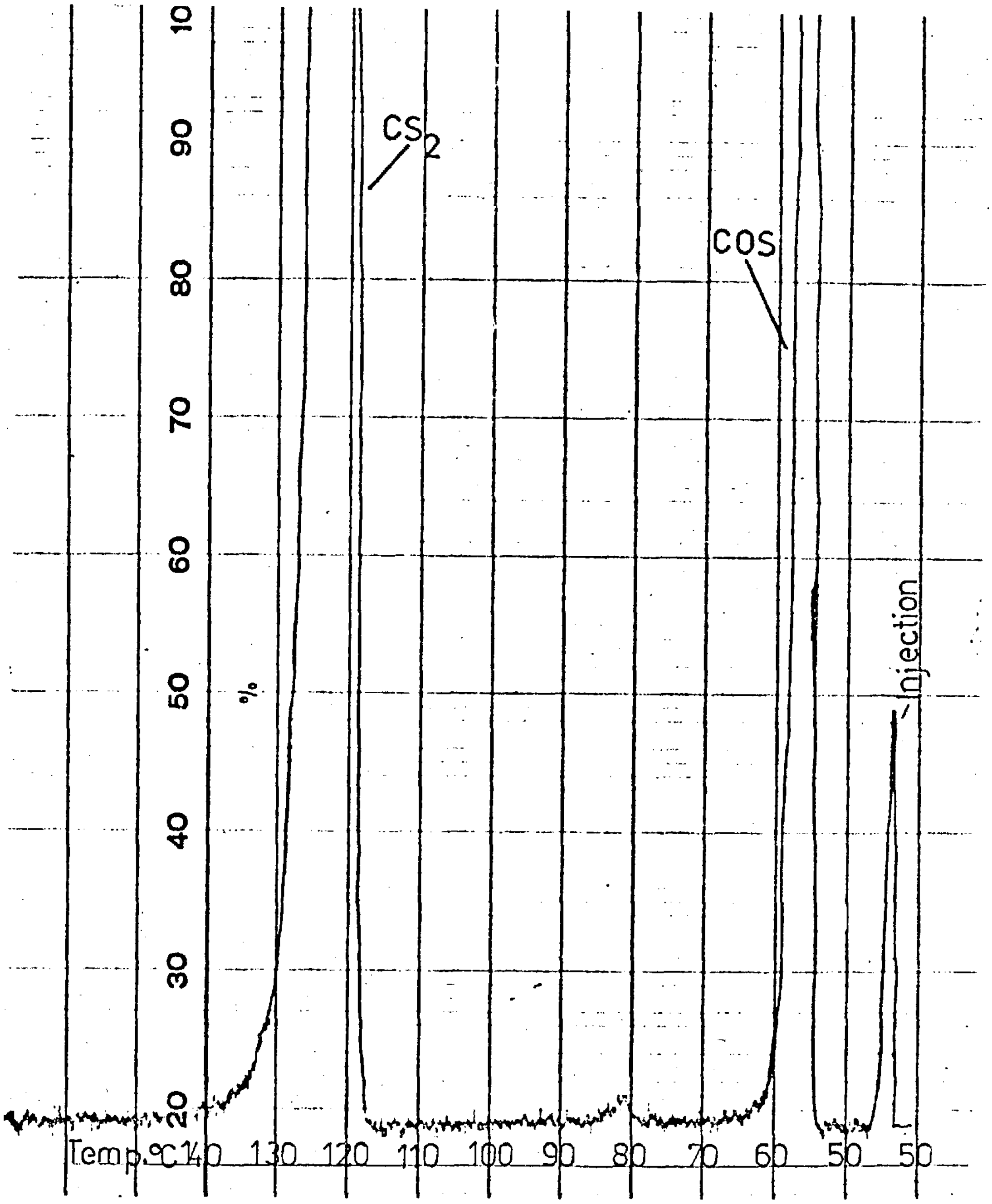

Fig. 7.21 Chromatogram showing presence of carbonyl sulphide and carbon disulphide in the head-space gas over a sterile sample of a Trefriw dump near the entrance of the main adit (after six days incubation).

7.3.1.4 Conclusions.

The selection of a gas chromatograph with a sulphur specific detector as the chief analytical instrument for this work has proved to be justified. It has been possible to demonstrate that, under laboratory conditions, oxidizing sulphides do not appear to generate either sulphur dioxide or hydrogen sulphide. This result strongly confirms the earlier experiments using chemical methods which were unable to detect either gas near oxidizing sulphides in the field. Ths gas chromatograph has, however, permitted the detection of other gases over sulphide minerals, the principal ones appearing to be carbonyl sulphide and carbon disulphide.

Sulphur dioxide has only been detected over freshly crushed pyrite and hydrogen sulphide has never been detected any conditions. Carbon disulphide and carbonyl sulphide have been detected over a wide variety of sulphide minerals including pyrite, galena, chalcopyrite, arsenopyrite, stibnite and jamesonite. Furthermore, these gases are produced in greater quantities when the sulphides are wet rather than dry.

It has been shown that the problems of collecting sub-nano gramme quantities of sulphur gases, present in the parts per billion range in gas mixtures presents very great difficulties especially as the methods to be used must be practical for field use.

The typical odour of oxidizing sulphides such as that present in the atmosphere a Trefriw remains to be explained. It is probable that the odour is a synergistic physiological response to a wide range of sulphur gases, rather that to a single gas.

The role of bacteria in the production of sulphur-bearing gases from sulphides remains ambiguous. The results of preliminary experiments on sterilized and unsterilized samples indicated little difference in the gases evolved but the very nature of the gases is suggestive of bacterial activity.

Sulphur-bearing gases have been shown to be released from soils and the initial results suggest that the quantities may be greatest in areas where the soils are closely associated with sulphide mineralization. This approach may have considerable merit in terms of speed and convenience and would eliminate many of the problems that currently exist in collecting soil-gas as such.

Passive sampling methods which have been successfully applied by M. Hinkle in the Nevada desert are difficult to use in the wetter conditions encountered in this country. Of the two active sampling adsorbents tested so far Tenax GC appears to be the more promising with the current desorption and presentation method.

CHAPTER 8

SUMMARY OF PRINCIPAL CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

8.1 Summary of Principal Conclusions

The research reported in this thesis has, of necessity, been of a preliminary nature as it is concerned with a relatively new and interesting aspect of exploration techniques. However, it is felt that the following provisional conclusions can be drawn from the results to date.

(1) It has been shown that, contrary to other workers published findings, hydrogen sulphide and sulphur dioxide, do not have any general application in the search for buried ore deposits. Sulphur dioxide has only been detected over sulphide dumps in strong sunlight. This is despite many modifications to existing wet chemical methods which improved their sensitivity, efficiency and convenience. These results are in agreement with complementary research being carried out by the US Geological Survey.

(2) Gas chromatography has been shown to be a far more powerful tool in the investigation of sulphur gas geochemistry than the wet chemical methods for specific gases.

(3) The principal gases evolved from oxidizing sulphides under laboratory conditions have been satisfactorally identified by gas chromatography as carbonyl sulphide and carbon disulphide. This work has confirmed our initial investigations which indicated the absence of hydrogen

sulphide and sulphur dioxide; the only exception was that sulphur dioxide was detected in appreciable quantities over freshly crushed pyrite under laboratory conditions.

(4) Dimethyl disulphide has been detected in headspace gas over sulphides under wet conditions.

(5) The role of bacteria in the formation of sulphur gases has yet to be shown to be important. Initial experiments suggest, surprisingly that their role may be of little significance. Further work is required.

(6) Soil gas sampling as such, either by active or passive means has been shown to be fraught with many difficulties and the soils themselves may well prove to be a more attractive sample medium. Furthermore it would appear that passive sampling, at least in its present form, will be difficult to apply in wet, temperate conditions.

8.2 Recommendations for Future Research

It is recommended that, following the essential primary investigations described in this thesis, the following research should be undertaken.

(1) Continued development of the application of gas chromatography coupled with a flame photometric detector to sulphur gas geochemistry. The objectives will be to quantify the results, and to develop the methods towards more rapid analyses.

(2) The investigation of the parameters which control the formation and dispersion of sulphur gases. This work should include both field trials and laboratory experiments using artificial soil/sulphide systems.

The addition of a katharometer to the gas chromatograph would greatly assist the laboratory experiments as it would then be possible to monitor the rate and effects of oxygen comsumption and carbon dioxide removal or production.

(3) The use of the soils themselves as a sampling medium should be given special attention. Field work should include investigations in both mineralized and non-mineralized areas with particular efforts being made to establish optimum sampling depths and techniques and appropriate development of sample preparation and treatment. Bulk sampling is recommended as a means of establishing these parameters and as a means of determining the repeatability and confidence of the methods.

(4) Although with a reduced emphasis, soil gas and atmospheric sampling using adsorbents should continue. This work will entail some development of the adsorbents and of conditioning, storage transport, desorption and presentation techniques. Passive sampling should be confined to areas of limited rainfall.

(5) In order to characterize the odour of oxidizing sulphides gas collection at Trefriw or similar area is recommended. Cold trapping of the samples using

liquid nitrogen is suggested followed by analysis by both gas chromatography and mass spectrometry.

(6) Simultaneous operation of the detector in both the flame photometric and flame ionization mode would permit a fuller study of the entire range of gases, including hydrocarbons, that are evolved by, or adsorbed onto, soils.

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