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EVALUATION OF THE ANALYTICAL POTENTIAL OF

AUGER ELECTRON SPECTROMETRY

IN ATMOSPHERIC ANALYSES

by

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A Master's Thesis

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ABSTRACT

The scope of this study into the analytical potential of gas phase Auger electron spectrometry (AES) is defined, and its relation to the work previously conducted at the University of Technology, Loughborough on this topic is shown.

The vacuum generators AFM2 gas phase Auger electron spectrometer is described in detail, this includes a discussion of maintenance and fault-finding. Detailed operating instructions based on the manufacturer's manual and the author's experience, are included. The theoretical and experimental aspects of the operational parameters of the electron gun, analyzer, detector, sample introduction system, and the recording system are given. The choice of parameter values for the optimal performance of the instrument are discussed.

Experimental work centres on the qualitative and quantitative analysis of the gases normally found in atmospheric air.

The section dealing with qualitative analysis includes a description of the Auger spectrum, the Auger process, and spectral interpretation. Experimental work included obtaining spectra for N_2, O_2, Ar, Ne, H_2S, SO_2, CO, CO_2, NO, NO_2, N_2O, NH_3, CCl_4, and several gas mixtures. Elemental and molecular analysis of pure gases and mixtures is discussed.

Quantitative analysis of gases using AES is a new field of study therefore nomenclature, symbols, units, errors, counting statistics, figures of merit and limits of detection for AES are defined and discussed. Experimentally determined sensitivities and limits of detection for the previously mentioned gases were obtained. Analytical calibration curves for each gas in a binary mixture are shown. A three component mixture is used to assess the use of an internal standard and to determine the presence of matrix absorption.

The design and operation of a vacuum system for the preparation of gas mixture standards is described together with modifications of the instrument sample inlet system and the method of measuring signal intensity.

Lastly a number of possible instrument modifications, suggestions for future work, and comparisons of the technique to present instrumental methods of gas analysis are discussed.

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Chapter 1

INTRODUCTION

Pierre V. Auger[1] was the first person to investigate the radiationless emission of electrons from materials bombarded by x-rays. His work took place in 1925, however it was not until 1953 that Langer[2] proposed that these Auger electrons could be put to a practical use in determining the surface composition of solids. The method of electronic differentiation was used by Harris[3] who demonstrated the high sensitivity attainable and the practicality of the technique for surface analysis. Scheiber and Tharp[4,5], and Weber and Peria[6] showed the feasibility of using the profusion of low-energy electron diffraction (LEED) instruments available at that time for Auger spectrometry in the differential mode. In 1969 Palmberg, Bahn and Tracy[7] showed that the coaxial electrostatic analyzer was more sensitive than previous analyzers and hence increased the speed for analysis. These developments have lead to Auger electron spectrometry (AES) becoming an invaluable analytical tool for surface analysis. Not only can elemental analysis be performed but information concerning the chemical environment of surface atoms can also be obtained.

AES is however, not only a surface technique. It has also been used to study gases; the high resolution possible for measuring the electrons ejected from a gas target and the simpler conditions of gas analysis have made the study of the Auger spectra of gases an area for fundamental research. Mehlhorn[8] was the first to show the advantages of studying the Auger spectra of gaseous atoms with high resolution. Studies on the rare gases by Siegbahn et al.[9,10] and Krause et al.[11]; and small molecules such as N_2[12 - 16], O_2, NO, CO, CO_2, and H_2O[9,14,15], C_3O_2[17], fluorinated[14] and brominated methanes[18] have been done. In 1974 Thompson et al.[19] suggested that there was an analytical potential for AES in the gas-phase. The gases studied by Thompson et al.[19,20] included C_2H_2, C_2H_4, H_2S, SO_2, NH_3, CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. Additionally the following gases have been studied CH_4[18,21]; N_2O[22]; NH_3[23]; H_2S[24], SO_2, and SF_6[25]; and HF, CH4, H2O, and CO.[26]

A bibliography[27] of AES literature from 1925 to 1975 has been published. More than seventy reviews of the literature are available; those by Thompson[28,29] and Hercules[30,31] review the AES literature thought to be of particular interest to analytical

chemists. A text by Davis[32] briefly discusses the qualitative and quantitative aspects of surface analysis by AES. Carlson[33] in his text on photoelectron and Auger spectroscopy has discussed AES for use in gas analysis; he states " As yet, no systematic study of its analytical possibilities on gases have been made, but it would appear to be a worthwhile undertaking."

The analytical potential of vapour-phase Auger electron spectrometry has been studied at the University of Technology, Loughborough, since 1975. The two previous theses[34,35] on these studies have reported on a wide range of topics related to AES and have established the need for a systematic study of the analytical potential of AES of gases.

Experimental work previously conducted[19,20] has centered on the acquisition and interpretation of high resolution Auger spectra of pure gases. This thesis reports the results of an investigation into the analytical potential of the technique as a tool for elemental and molecular analysis of pure gases and gas mixtures. Both qualitative and quantitative studies have been conducted; the quantitative studies are the first reported. The analytical system chosen to examine this potential has been the gases commonly found in the atmosphere. It has not been the intent to determine a method of atmospheric analysis, but to use atmospheric gas analysis as the analytical system to pursue these studies.

Fig. 2.1. The AFM2 Vacuum Generators gas phase Auger electron spectrometer.
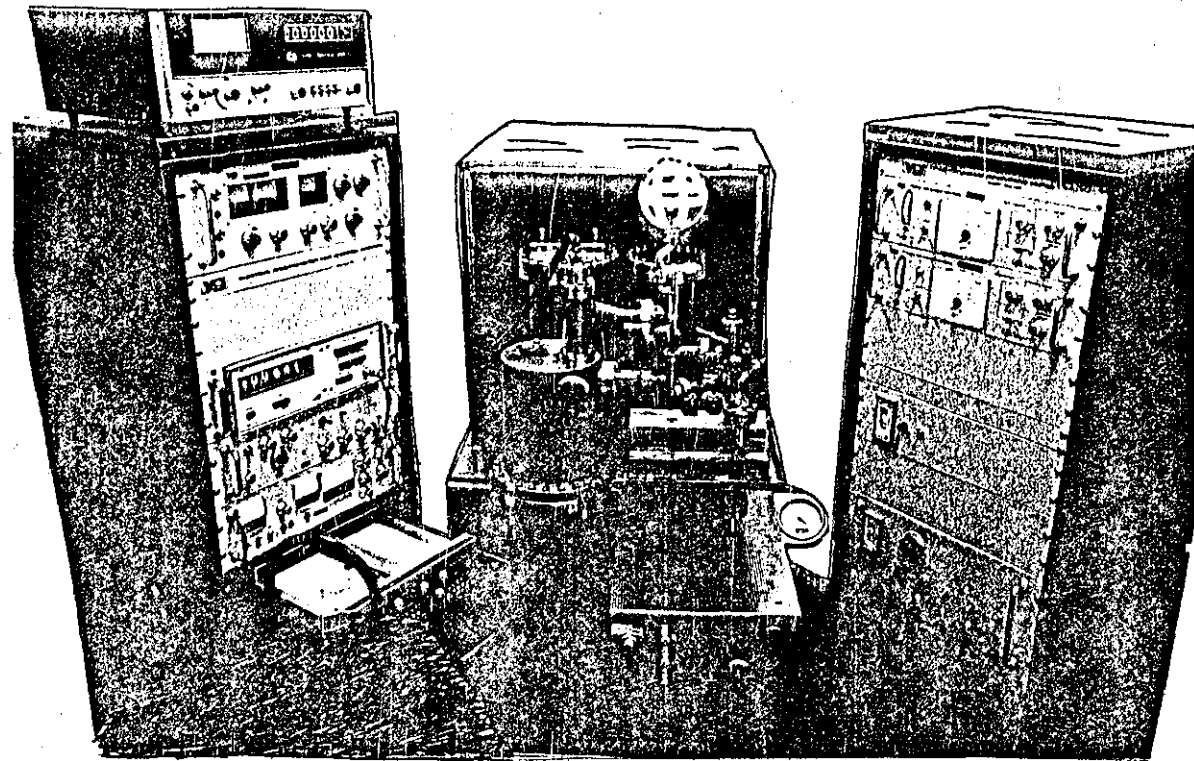
Spectrometer Control
Console

Spectrometer and
Vacuum Systems

Vacuum Control
Console

Chapter 2.

THE VACUUM GENERATORS   AFM2

AUGER ELECTRON SPECTROMETER

FOR GASES

2.1.   Introduction

This spectrometer is a hybrid instrument which was adapted
from the Vacuum Generators (VG) ESCA system. The original instruc-
tion manual, which was an alteration of the ESCA manual, did not
adequately cover the operations to which the instrument has been
applied. The instrument has also been difficult to operate ever
since installation. This chapter has therefore been written to
provide an up-to-date and purpose conscience manual. The manner
in which it is written has been chosen to be of most use to sub-
sequent uses; this may in places be at the expense of the style
normally expected in a thesis of this type.

The spectrometer was installed at Loughborough University
of Technology on 19.3.75 and has been used by two previous post-
graduate students. It has been described in two theses [1,2] and
in one paper [3]. Fig. 2.1 is a photograph of the instrument,
detailed diagrams of the components are shown in the various figures,
Figs. 2.4 and 2.8 show the main components. The instrument is com-
prised of an electron gun, gas introduction system, collision
chamber, electron energy analyzer, electron multiplier and pumping
equipment. The electron gun operates up to 5 keV beam energy and
has a controllable emission current and focus. The electron beam
passes through a differential pumping system into the gas collision
chamber which is operated at a higher gas pressure. Electrons
arising from electron-gas collisions pass out of the chamber,
through a variable entrance slit and into a 150° hemispherical
analyzer which is fitted with an electron multiplier. Additionally,
the electrons are retarded to a specific energy prior to analysis
and counting.

The general mode of operation is to allow the analyte gas
to leak from the sample container into the collision chamber while
maintaining an appropriate pressure in the analyzer and electron
gun chambers. The various operational parameters of the system are
then set for maximum signal-to-background ratio for the most intense
Auger peak of the spectrum. The spectrum is then recorded or an
intensity measurement is made.
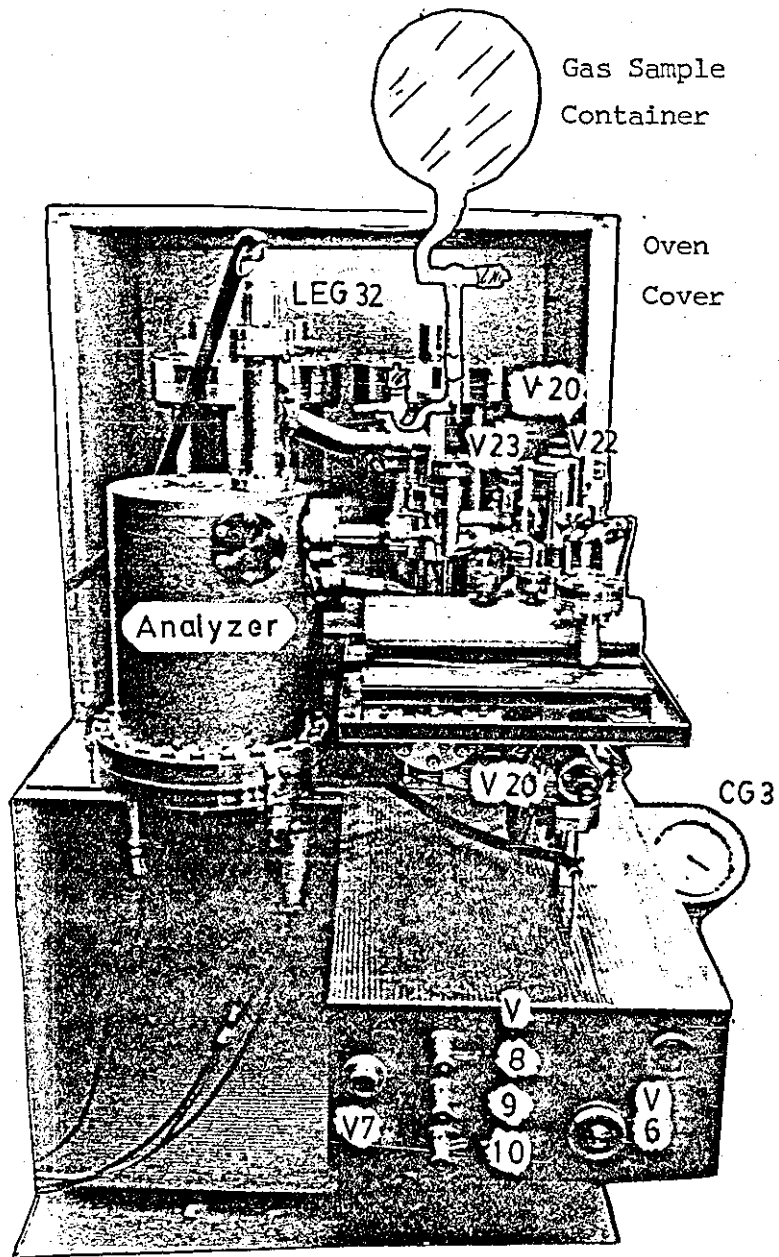
Fig. 2.2. Front view of the vacuum system and spectrometer.
(Refer to Fig. 2.4 for component names.)

Information included in this chapter comes from the instrument log book, the VG instruction manual, various VG and component manuals, product literature, from numerous discussions with Dr. F. Tothill of Vacuum Generators Ltd. and from the author's experience with the instrument.

2.2. The Vacuum System

2.2.1. General

The system consists of an assembly of standard vacuum components and purpose built components. The photographs in Figs. 2.2 and 2.3 show the vacuum system. Fig. 2.4 is a diagram showing more detail of the connections between the components. It is probably a more useful diagram than previously available as it shows the components in approximately the positions they occupy when viewed from the front of the system.

There are actually two vacuum systems, the high vacuum/spectrometer system and the rough pumping/gas handling system. The rough pumping system is used initially to reduce the pressure in the spectrometer to ca. 0.01 torr before the high vacuum pumps can be used. The usual application of the roughing system is to evacuate the sample handling system before each sample is admitted. The high vacuum system maintains the pressure in the spectrometer and the electron gun at a value down to 10^{-9} torr.

The rough pumping system consists of a rotary vacuum pump, the appropriate valves, a built in one litre sample container and a one litre sample expansion chamber. Gases can be admitted through three valves (V8, V9, V10) into the litre container. This however has proved to be inconvenient as special glass-metal connectors must be added to sample containers which are then mounted under the instrument. In addition, leakage of air occurs at the joint between the sample container and inlet port. Therefore an inlet valve on the expansion chamber has been modified to accept a flask with a B14 glass joint. Both the air leakage problem and the inconvenience of the original design are thus overcome. In addition less gas is required as only the sample expansion chamber need be used, although the one litre container may also be used. In order to determine the pressure of the gas sample the expansion chamber has been connected directly to the vacuum guage (CG3). Another problem in the rough pumping/gas handling system is the valve (V24) which admits sample gas into the spectrometer. The inability of the valve to maintain a constant electron gun gas pressure (and flow rate into the
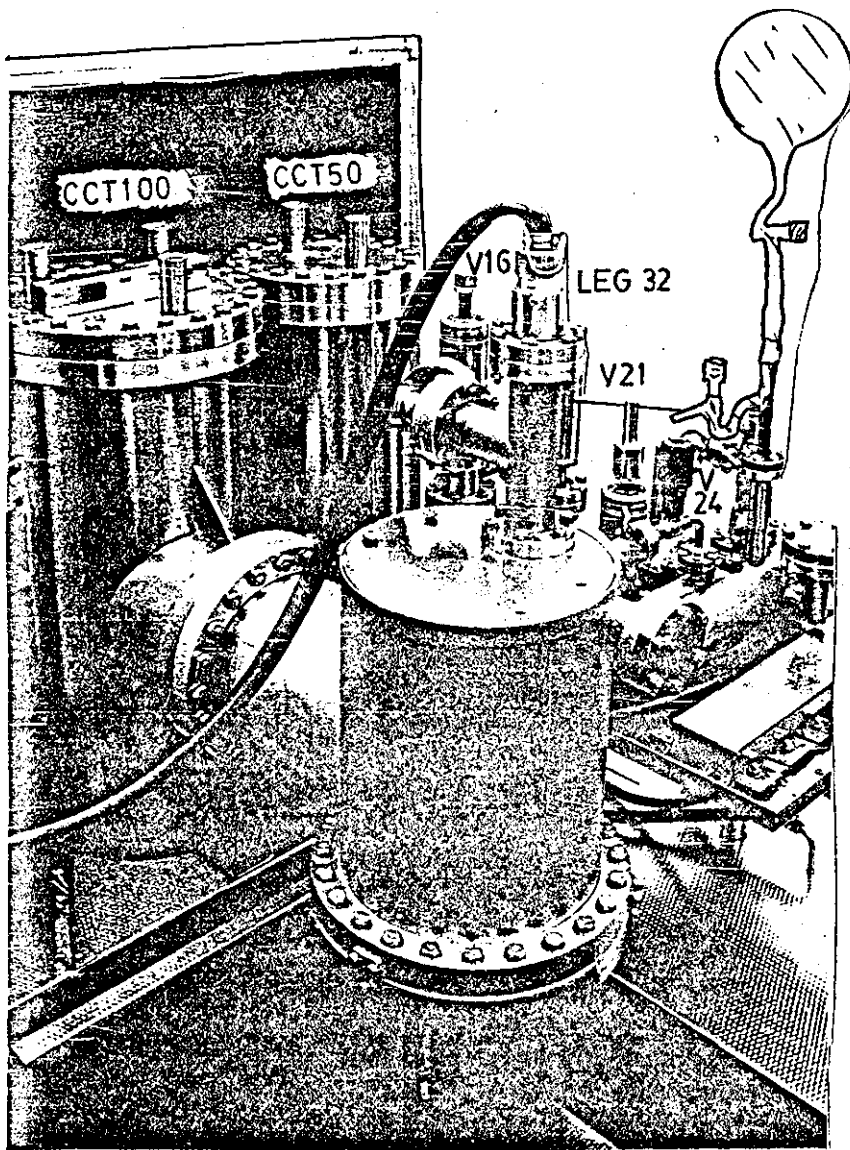
Fig. 2.3. Side view of vacuum system and spectrometer.
(Refer to Fig. 2.4 for component names.)

HIGH VACUUM SYSTEM

ED 330

ED 50

ROUGH PUMPING SYSTEM

V11

V13

V12

CCT 100

CCT 50

VSK1 PVGI(1)

RT1

EO4

EO2

V6

VIG20(1)

VIG20(2)

V1

V16 V20

LEG32

S

V5

S

CG3

V23 V21

PVGI(2)

SPECTRO-METER

V24

EXPANSION CHAMBER

V7

V22 CG3

V10 V9 V8

S S S
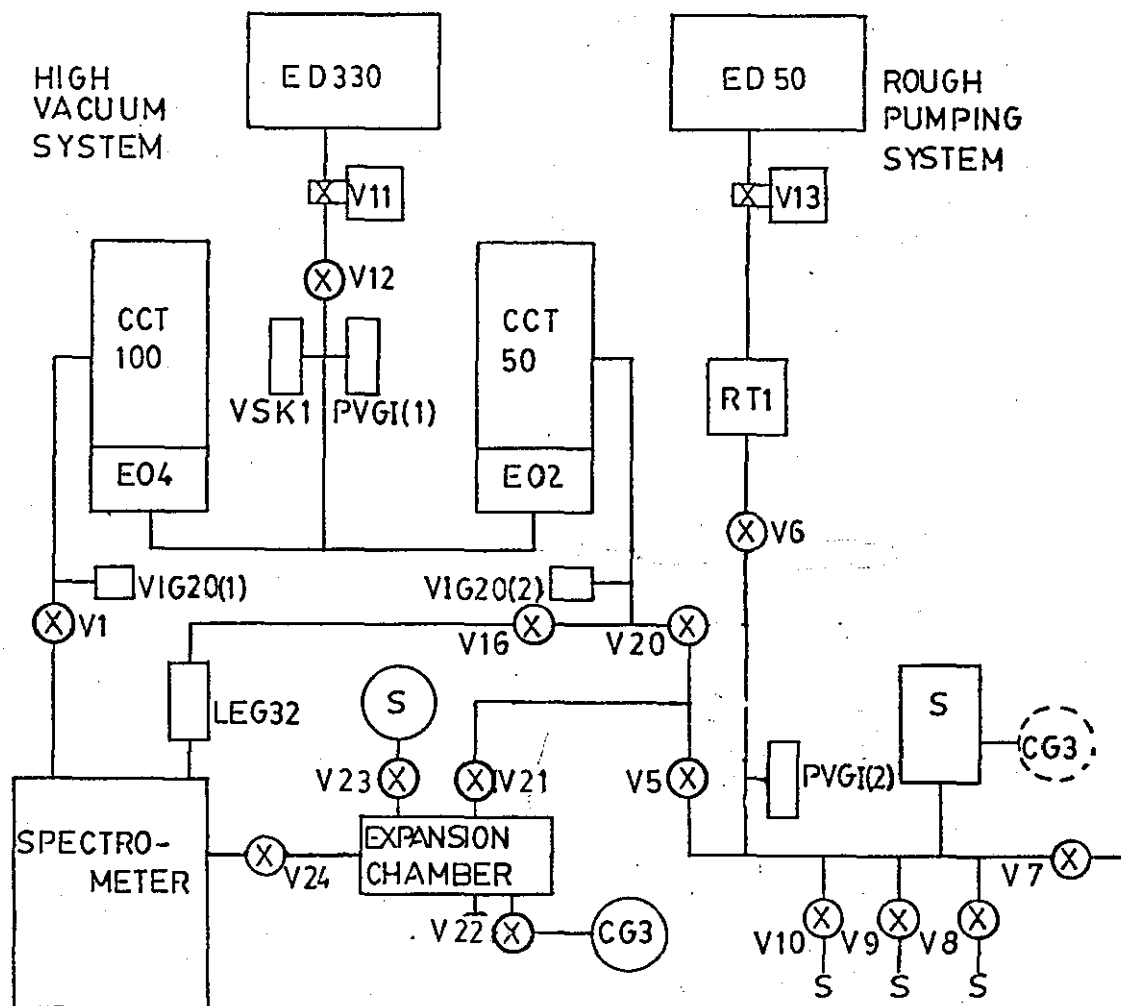
ED330	Backing Pump	ED50	Roughing Pump
V11	Solenoid Isolation Valve	V13	Solenoid Isolation Valve
V12	Manual Valve		
VSKI	Pressure switch inter-locked with ED330	RT1	Sorption Trap and heater
PVGI (1)	Pirani Gauge Head	V6	Manual Valve
EO4)	Spectrometer / Electron	PVGI (2)	Pirani Gauge Head
EO2)	Gun Diffusion Pump	V8, V9, V10	Sample Gas Inlet Valves
CCT100) CCT50)	Combination Cold Traps	V7	Air Inlet Valve
VIG20 (1)	Spectrometer / Electron	V5, V21	Sample Chamber Roughing Valve
VIG20 (2)	Ionization Vacuum Gauge		
V1	Spectrometer Isolation Valve	V23	Sample Inlet Valve
		S	Sample Container
V16	Electron Gun Isolation Valve	V22	CG3 Valve
		CG3	Sample Pressure Gauge
LEG32	Electron gun		
V20	Sample Chamber H.V. Pumping Valve	V24	Sample Control Valve

Fig. 2.4. The vacuum system of the AFM2 Auger electron spectrometer.
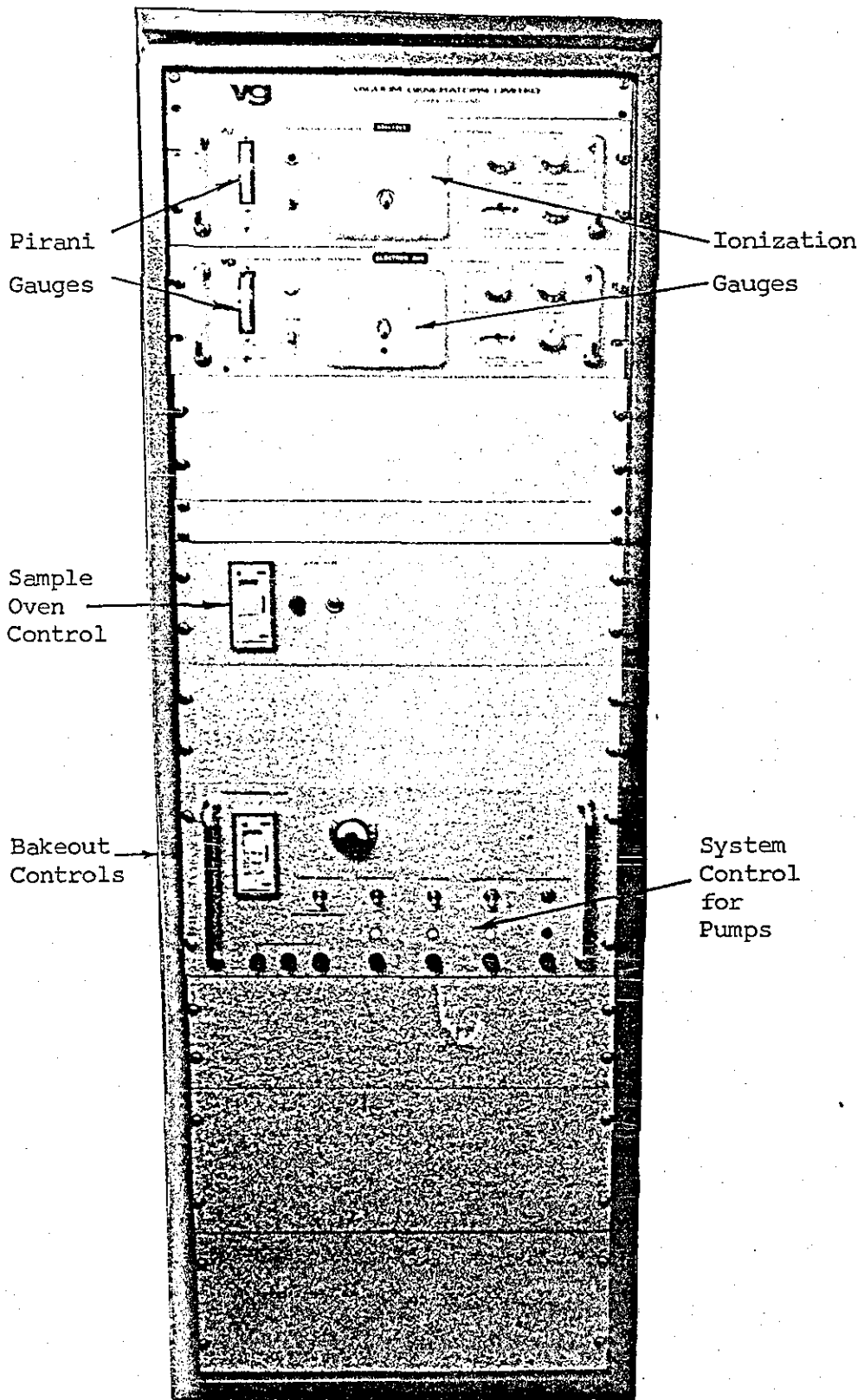
Fig. 2.5. Vacuum instrumention console.

spectrometer) limits reproducibility of analyses.

The high vacuum system consists of a larger capacity rotary pump, two oil diffusion pumps, the appropriate valves, two ionization vacuum guages, a Pirani vacuum guage, and the spectrometer and electron gun. The larger diffusion pump, pumps the spectrometer while the smaller pumps the electron gun. The electron gun is connected to the spectrometer by a differential pressure system (Fig. 2.10). Thus the gun and spectrometer can be maintained at different pressures. This is necessary as the gun has a maximum operating pressure of 5×10^{-7} torr.

The vacuum systems can be baked at temperatures up to 230°C. Baking is necessary to achieve the lowest pressures possible with the system and to rid it of samples which may have condensed or absorbed on internal surfaces. Water vapour sorbed on the walls of the vacuum system is a usual problem after the system has been let up to atmosphere. All of the components above the table top are baked in a detachable oven hood.

The vacuum instrumentation is contained in a 19 inch console (Fig. 2.5). It consists of two combined ionization and Pirani controllers, system control for pumps and bakeout and a sample oven control. The controllers indicate ion guage pressures in the range of 10^{-3} to 10^{-9} torr and Pirani guage pressures of 0.5 to 10^{-3} torr. Filament trip-out (ion-guages) is adjustable to operate anywhere within the range of the instrument. Filament degassing is controlled from the controller. Two controllers are used. One measures the pressure in the spectrometer stack and the diffusion pump backing system. The other measures pressure in the electron gun stack and the roughing line/gas handling manifold.

The system panel incorporates switching for the rotary and diffusion pumps and control of the vacuum system bakeout. It also incorporates a Eurotherm temperature controller. The sample oven controller controls the temperature of the sample expansion chamber and the sample collision chamber in the spectrometer.

2.2.2. Vacuum System Components

The component numbers are from Fig. 2.4. Instruction manuals are listed in Appendix A.

ED330   Backing pump for the high vacuum/spectrometer system.
               Edwards high speed rotary pump. 330 litres per
               minute displacement. The pumping mechanism is of the

Liquid nitrogen filler ports

Ionisation
gauge port

Liquid nitrogen reservoir

Narrow gap —
causes released vapours to be recondensed

System
flange

Valve handwheel

Pneumatic actuator
(when fitted)

Chevron array

Bench
mounting
brackets

Water-cooling

Baffle

Pump flange

Fig. 2.6.   Combination cold trap.

DRIVE SCREW NUT
DRIVE SCREW
COLLAR
DRIVE SCREW

GUIDE SLEEVE

BALL BEARING

PLUNGER
BELLOWS

GOLD PLATED
COPPER PAD

STAINLESS
STEEL
KNIFE EDGE
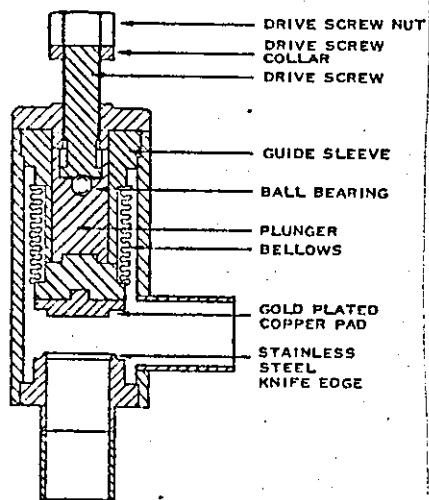
Fig. 2.7.   All metal bakable valve.

slotted rotor/sliding vane type. Each of the two stages has separate rotor assemblies operating in a common stator with interconnecting port. A gas ballast facility is also incorporated to prevent contamination of the oil by the vapour being pumped.

VII   ED330 isolation valve. The one inch magnetic valve opens and closes the high vacuum pipeline. It consists of a cylindrical metal case containing a solenoid activated plunger which opens a passage between two ports in the body. It will seal against atmospheric pressure in either direction, leakage is less than 10^{-6} torr s^{-1}.

V12   Manually operated backing line valve. Edwards one inch Viton sealed speedivalve.

VSK1   Backing line pressure switch interlocked with diffusion pump heaters.

PVG1 (1)   Backing line all metal Pirani guage head.

EO4   Spectrometer diffusion pump. Model EO4 Edwards oil vapour diffusion pump. Peak air speed is 600 litres s^{-1}, ultimate vacuum is less than 10^{-9} torr with Santovac 5 oil (polyphenyl ether).

EO2   Electron gun diffusion pump. Peak air speed is 150 litres s^{-1}.

CCT100   A combination cold trap for EO4. The trap contains both water cooled baffles and liquid nitrogen cooled chevrons. It enables an oil diffusion pump to attain ultimate pressures of 5×10^{-11} torr. (Fig. 2.6)

CCT50   A combination cold trap for EO2.

VIG20-1   Analyzer vacuum ionization gauge.

VIG20-2   Electron gun vacuum ionization gauge.

V1   Spectrometer isolation valve, viton sealed, incorporated in CCT100. (Fig. 2.6)

V16   Gun to EO2 stack isolation all metal valve. (Fig. 2.7) same as V5, V20, V21.

LEG32   Electron gun and the differential pumping system between it and the spectrometer. (Fig. 2.10)

ED 50	Vacuum pump for the rough pumping/gas handling system. Edwards two stage 50 litres per minute displacement. Refer to ED330.
V13	ED 50 isolation valve, Edwards $\frac{1}{2}$ inch solenoid valve. Refer to V11.
RT1	Sorption foreline trap with integral heater. 260g. charge of moleculor sieve 10A or 13X.
V6	Gas handling manifold roughing valve. Vacuum Generators model VRD25 Viton sealed valve.
V5	Sample expansion chamber roughing valve. Vacuum Generators model CR25 all metal valve. (Fig. 2.7) Same as V6, V20, V21.
V7	Air admittance valve. Vacuum Generators model GH7, Viton sealed valve.
V8 V9 V10	Sample gas inlet valves. The gas admission lines terminate in Edwards $\frac{1}{4}$ inch screwed vacuum unions. Edwards model OSID Viton Sealed needle valves.
PVGI (2)	Rough pumping line and gas handling manifold, all metal Pirani gauge head.
CG3	Calibration gas pressure gauge. Capsule dial type 0 to 20 torr.
V20	Sample expansion chamber high vacuum pumping valve. Refer to V5.
V21	Sample expansion chamber pumping valve. Refer to V20.
V22	Valve to CG3 vacuum gauge. VG modified design, Hoke stainless steel bellows sealed valve type 4172G4Y, fitted with extension pipes and mini FC flanges.
V23	Sample inlet valve. Refer to V22.
V24	Sample control valve into spectrometer collision chamber. Refer to V22.

2.2.3. Operation of the Vacuum System

The instructions in this section assumes that the system has been properly set-up and is functional. If this is not the situation then reference should be made to sec. 1.2, Installing AFM2, of the original instruction manual.

Operation of the vacuum system is straight forward and should not be a source of problems. Instructions begin with the start-up of the system.

Preliminary Checks

Check that the cooling water supply is turned on. The flow rate should be about $3\frac{1}{2}$ litres per minute. Checks for water leaks should be made. As no electrical power is on water will not be fed to the circuits having solenoid valves so additional checks will be required later.

Before switching on the main supply, all switches on the consoles should be in the OFF position. The bakeout timer should read ZERO and the "power bakeout/power instrument console" switch should be in the POWER BAKEOUT position. All hand operated valves should be closed (turned fully clockwise). Switch ON at the mains.

Starting the Backing and Diffusion Pumps

The backing pump (ED330) is then switched ON, a red lamp lights on the console. A relay operates to start the pump; solenoid valve V11, interlocked with the pump, opens. Opening the backing valve, V12, allows the diffusion pump stacks (CCT100 and CCT50) to be rough pumped.

Set the diffusion pump switch to the ON position. This causes a relay to operate turning on both diffusion pumps (EO4, EO2). The diffusion pump red indicator lamp lights provided the backing pressure is low enough to operate pressure switch VSKI and that the thermal switch on diffusion pump EO4 is closed. The function of VSKI is to switch off the diffusion pumps if the backing pressure rises above 100 torr.

Ensure that the "read pressure" switches on the two vacuum gauge controllers are OFF. Switch ON both units, mains power is available only when the diffusion pumps are on, the mains indicator lamps should light. The backing pressure can now be read on the "Analyzer" Pirani gauge, PVGI (I). The pressure should be less than 0.1 torr. If it is greater then the diffusion pumps should be switched OFF and the leak investigated. Refer to sec. 2.2.4 for instructions on locating and correcting leaks.

Water leaks should now be checked for in the remainder of
the water circuit. When the diffusion pumps have been on for
twenty minutes, turn ON the ionization gauges by setting the
"read pressure" switch to the 4 mA emission level on both con-
trollers. Read the pressure on each. The pressures should be
less than 10^{-5} torr. Turn OFF the ionization guages. If the
pressure was unsatisfactory correct the leaks and recheck.

Rough Pumping

Check that all remaining valves are closed. Switch ON
the roughing pump. Solenoid valve V13, interlocked with the pump
opens and the red pump indicator lamp lights. Open V6 to rough
pump the gas handling manifold. The pressure indicated on the
Pirani gauge of the electron gun vacuum control unit should rapidly
fall to approximately 0.01 torr. If there are no leaks then pump
out the sample expansion chamber by opening valve V21. The
pressure on the Pirani gauge will rise but should again fall to
0.01 torr if there are no leaks. To pump out the spectrometer,
the Hoke valve, V24, is slowly opened. The indicated pressure will
rise but again should eventually drop to 0.01 torr.

Pumping to High Vacuum

All leaks must have been corrected and the pressure
should be approximately 0.01 torr. Close V5 to isolate the
spectrometer and sample expansion chamber from the gas handling
system. The ionization gauges should be switched OFF. Slowly
open V20, V16, and V1. Wait a few minutes before measuring the
pressures. After setting the filament trip-outs to ca. 10^{-4} torr
switch ON (4 mA position) both ionization gauges. Both gauges
should read less that 10^{-5} torr. The pressures may drop more with
time but the system will probably have to be baked to obtain
pressures of less than 10^{-8} torr. If the pressure is high the
sample expansion chamber should be isolated by closing V24 and V20.
If the pressure drops then the leak is in the sample expansion
circuit. Check that the Hoke valve, V23, is closed as the vacuum
guage, CG3, has a rubber O-ring. If the pressure is still high
then the remainder of the high vacuum system will have to be checked
for leaks.

Baking the System

Periodic bakeout is a convenient way of cleaning the system
to obtain the minimum operating pressure of the system. Bakeout
is required after the system has been let up to air and when the

operating pressure rises due to the analysis of volatile samples.

The condensation of water vapour and sample vapour on the internal surfaces will slowly impair the vacuum performance and may even affect the instrument calibration by modifying the work functions of the spectrometer surfaces.

Bakeout is conveniently done during the night. Selection of minimum bakeout times and temperatures allow the instrument to be used the following morning. High temperatures require a longer cool down time and also eventually damage valve threads and valve seats. An eight hour bakeout at 120° C is recommended, although temperatures up to 230°C may be used.

Switch OFF all supplies on the instrument console, remove the three connectors from the base of the spectrometer, and remove the electron gun connector. Set the "read pressure" switch on both ionization gauge units to OFF, but leave the gun unit ON. Unplug the vacuum gauge heads, remove all extraneous articles from the vacuum system table and raise the table under the spectrometer. Both the high vacuum pump and the roughing pump should be ON, and valve V6 open. Check that all valves above the table are open except those going to air and V5, the valve between the high vacuum system and the sample handling manifold. This valve is located just above the table and below the sample expansion chamber. If any valve needs to be opened, do so slowly. All valves on the sample handling manifold going to air should be closed. Remove the support bracket for the electron gun and the glass sample inlet system.

The large section of the oven is conveniently stored on the table over the rotary pumps and it can be rotated over the system (Fig. 2.2). The smaller section of the oven is conveniently stored on the floor behind the unit. It is put over the rear of the system and clipped to the first section.

Set the "power bakeout/power instrument console" switch to POWER BAKEOUT. Set the required temperature on the Eurotherm thermostat and set the timer for bakeout duration.

After bakeout the timer should have returned to zero. System temperature may be checked by putting the timer ON and slowly reducing the Eurotherm setting; the reading when the upper light goes out is the system temperature. If this is below 80°C the oven may be removed. Lower the table under the spectrometer and allow the system to cool. Do not operate the channel multiplier at a temperature above 70°C.

Switch to " Power instrument console" and switch on the DVM and instrument control unit after checking that the pedestal voltage is ZERO. This enables these items to stabilize before spectra are taken, the DVM requires a one hour warm-up.

Plug in both ion gauge heads, turn ON both control units, set the 4 mA position, and read the pressures. Both pressures should be similar and less than 10^{-6} torr. If the pressures are higher wait a few minutes and read them again. The sample expansion chamber may now be isolated, this may cause the pressures to drop slightly. If the pressures are too high check for leaks as indicated in sec. 2.2.4.

When the pressures are less than 10^{-6} torr set one unit on "Degas" at 10 watts. The heads must be degassed in order to give reliable pressure measurement below 10^{-6} torr. Check with the second unit that the pressure does not rise above 10^{-5} torr. The degassing power is usually increased to 25 watts if the pressure is 10^{-6} torr or less. The power can actually be increased to 100 watts if the pressure is less than 10^{-6} torr. The power should be turned up slowly while monitoring the pressure on the second gauge. A maximum power setting of 40 watts for 30 minutes is usually adequate. After one gauge head is degassed the process can be repeated for the second. Both gauges can then be switched to read the pressure (the 4 mA position). Both gauges should now read less than 10^{-8} torr, usually less than 10^{-9} torr. If they don't then leaks will again have to be corrected.

Letting the System Back to Air

The system will usually have to be let back to air when ever a component in the system is changed. If the component is in the sample handling system, then the remainder of the high vacuum system can be isolated and kept at high vacuum, otherwise the high vacuum pumps can be isolated and the remainder of the system let up to air. In case of complete shut down the entire system can be let up to air.

In letting only the sample handling system back to air the electron detector and the electron gun should be shut OFF. If the sample inlet valve happens not to be fully closed then the electron detector and electron gun could be damaged by high air pressure. Often if the spectrometer is at a pressure of ca. 10^{-9} torr then a rise in its pressure will be noted as the sample chamber is let back to air. For this reason it is best to have the sample chamber at as low a pressure as possible when measuring the spectrometer/gun

pressures for minimum pressure checks. Isolate the sample system from the high vacuum system by closing valves V24 and V20, and from the roughing pump by closing valve V6. Air may then be let into the system through valves V7 and V23, valves V5 and V21 should be open if the entire sample system is to be let back to air

In letting the sample system and the spectrometer back to air the detector, electron gun and all counting equipment must be switched OFF. Isolate the vacuum pumps by closing valves V1, V16, V20 and V6. Let the sample chamber back to air first. Then open the sample inlet valve (V24) and slowly allow the spectrometer back to atmospheric pressure. Pump down times may be decreased if the system is filled with dry nitrogen rather than air. However bakeout has always been found to be necessary before pressures of less than 10^{-8} torr can be attained.

Use of the Liquid Nitrogen Traps

Use of the liquid nitrogen traps was found to be unnecessary. They allowed a lower pressure to be obtained, particularly if the system either had not been baked out for awhile or if a slight leak was present. Their use apparently provided a higher pumping speed. However once they are used they either must be continued to be used or the system has to be bakedout. Otherwise the pressure normally rose to an unacceptably high value.

2.2.4. Maintenance and Precautions

Under this heading are included regular maintenance requirements, precautions in operating sensitive components, and techniques to be used for replacing gaskets etc.

Rotary Vacuum Pumps

The oil level in the sight glass should be checked monthly and refilled if necessary. The oil and filter should be changed every six months.

The belt tension should be checked the day after changing a belt and every three months.

The motor bearings should be lubricated every twelve months.

The pumps should be run occasionally with the ballast open to remove gases absorbed in the oil.

Vacuum System

A weekend bakeout will normally allow a minimum pressure to be maintained with a minimum of instrument down time. If a pressure of approximately 10^{-9} torr is not obtained after bakeout then the system should be checked for leaks.

Valves

The valves require no servicing, however the following pre-cautions are required to ensure a maximum life.

Don't bake with the internal structure exposed to atmospheric pressure.

Don't close a baked valve until it has cooled to ambient temperature.

Bakeout of a closed valve at temperatures above 300°C may cause a bond between the pad and knife edge.

Flanges and Gaskets

The flanges used are of the knife edge type. They compress a copper gasket located in recesses machined into each flange. If properly tightened a gas-tight seal is easily obtained. The technique used in tightening these flanges was to tighten each nut in turn as shown below. Each nut should be only "lightly snugged" in turn; as many as a dozen cycles will be required to fully tighten the flange.
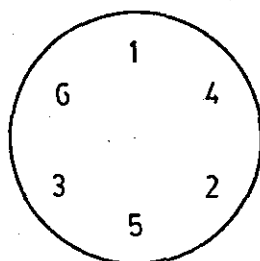
1st cycle 1-2-3
4-5-6

2nd cycle 2-3-1
5-6-4
etc.

Tightening Cycle for Flanges

The flanges must be tightened "squarely", check the gap between the flanges to ensure it is even all around.

Although it is recommended that the copper gaskets not be reused it has been found possible to reuse them on the same flanges.

2.2.5. Fault Finding

The major fault which occurs in the vacuum system is a gas leak. Other faults are associated with the ionization vacuum gauge and with the safety trip system.

Vacuum System Leaks

If a leak occurs in the system then the operations which have taken place prior to it should be recalled to determine a possible cause. An example is where the electron gun or some other component has been replaced and the vacuum system had no leaks prior to this operation. In this simple case then the flange or flanges which had been opened should be checked.

A sensitive check is to apply a small stream of helium to the flange and to note any change in pressure on the appropriate ionization gauge. A more sensitive technique is to encase the flange in a plastic bag and to fill the bag with helium. Having located the leaking flange then it should be checked to see that the mating flanges are "square" to one another. They should then be tightened using the procedure outlined previously. If this doesn't stop the leak then the gasket will have to be replaced. It should not be assumed, without testing, that the flange recently worked on is the one leaking; if a flange is over-tightened, bolts or nuts can be stripped.

In the case of a leak of unknown origin then the initial volume pumped should be isolated. If the pressure is sufficiently low than this volume should be opened to the next volume pumped, etc. In this way individual sections of the vacuum system may be checked until the leak is isolated.

A liquid leak sealing component has been found to be useful only in the case of leaks in the ceramic electrical feed-through of the electron gun. Gaskets are too inaccessable to the sealer, although it is useful if the flange is taken apart and the sealer can be applied directly to the gasket.

Valves are another possible source of leaks. The seats may wear or the bellows may leak. The valve would normally have to be replaced.

Ionization Vacuum Gauges

If a filament in the gauge is not working properly then the pressure reading will be unstable and the gauge will probably trip out. The filament will have to be replaced. However if sample pressure reading are normally taken on both the gun and the spec-trometer gauges then one gauge may suffice until it is convenient to replace the filament.

Safety Trips and Sequence Switching

Diffusion pump won't switch ON

- roughing pump may be off
- backing pressure is not sufficiently low
- cooling water supply is inadequate

The ionization gauges won't switch ON

- diffusion pumps are off

Scaler Timer

Electron Gun
Supply

Digital Voltmeter
" Auger Electron
          Energy "
Display

Analyzer
Control

Detector
Control
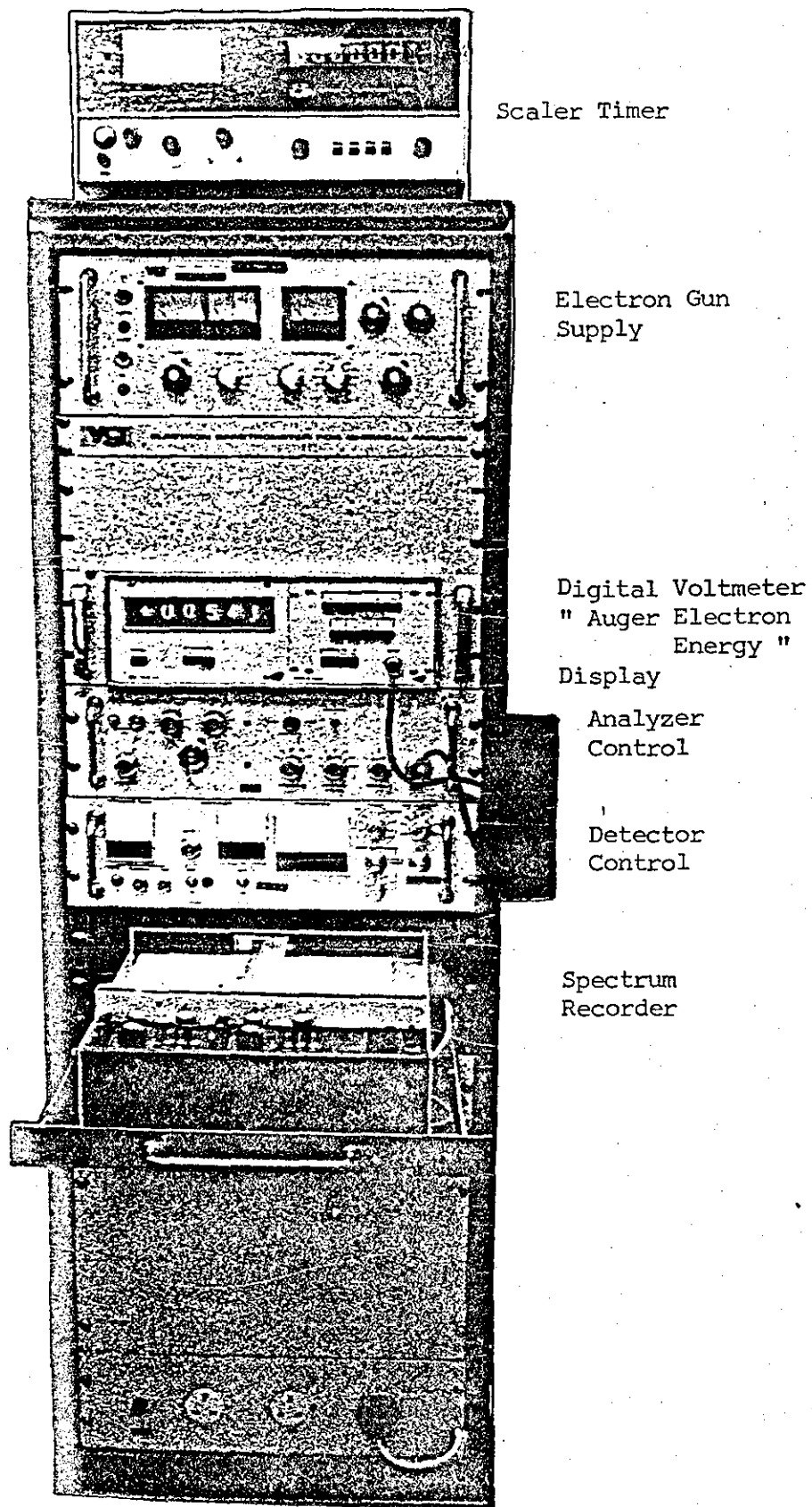
Spectrum
Recorder

Fig. 2.9. The spectrometer control console.

All circuits are de-energised

- rotary pump is switched OFF or is out because of a fault
  in the pump motor

Main instrument panel de-energised

- the gun ionization gauge controller is OFF
- the backing pressure in the diffusion pumps is too high
- cooling water failure to diffusion pumps
- ionization gauge tripped out due to a pressure rise

2.3. The Spectrometer

This section deals with the major components of the spectrometer. These are the electron gun, the collision chamber, the analyzer, the detector, and the output devices. (Fig. 2.8). A general description of each component, installation, operation and adjustment instructions, and problems areas are included for each. Fig. 2.9 shows the spectrometer control console.
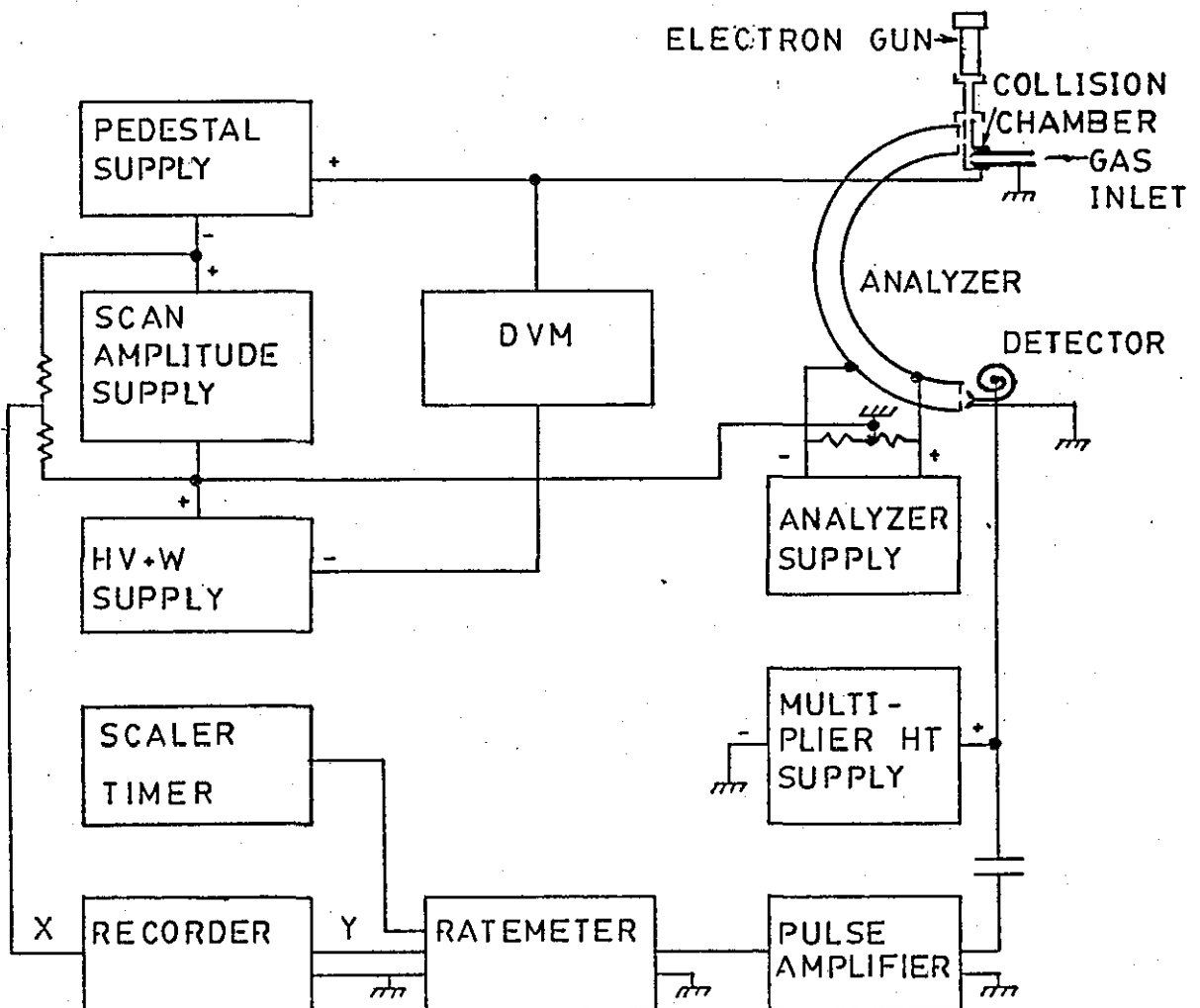
Fig. 2.8. The AFM2 Auger electron spectrometer.
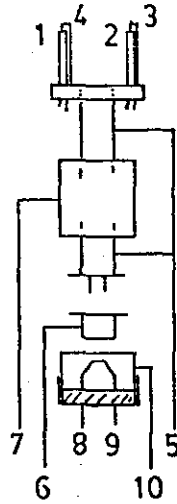
Fig. 2.10. The LEG 32 electron gun and pin connections.

ELECTRON GUN CHAMBER

COLLISION CHAMBER
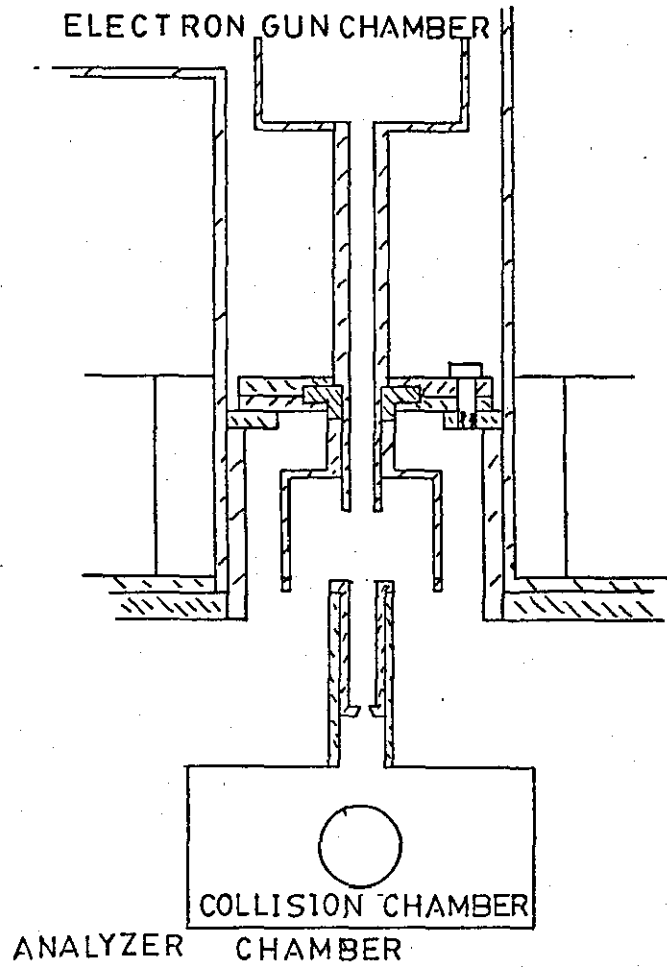
ANALYZER CHAMBER

Fig. 2.11. The differential pumping system between the analyzer and electron gun chambers.

2.3.1. The Electron Gun

The LEG32 electron gun (Fig. 2.10) produces a beam of energenic electrons used for excitation of the gaseous sample. It operates up to 5 kV beam energy, has a controllable beam current of up to 1 mA and a beam spot size of 15 μm. A low gas pressure is essential for preventing electrical shorting and for helping to preserve the filament life. The gun and the analyzer chamber are therefore connecting by a differential pumping system. The gun is normally operated at a pressure of less that 5×10^{-7} torr. A quadrupole arrangement on the end of the gun, controlled by X and Y controls on the panel, allow the electron beam to be centralized through the pumping tubes to the collision chamber. The final anode of the gun is referenced to the retard potential of the pedestal and scan amplitude supplies, this allows the electron energy to remain constant for all kinetic energies.

Installation

The gun is mounted on a flange and fits inside a mu-metal tee piece which is mounted on top of the analyzer chamber (Fig. 2.11). Four locating springs on the end of the gun position it correctly in the differential pumping tube.

The filaments in the gun have to be replaced frequently. The normal useful life under the conditions used for these studies has been approximately 100 hours. When the maximum beam current fell to 200 μA the filament was replaced. At this stage filaments were found to be deformed and "shrivelled". Fig. 2.10 shows the electron gun pin connections. These should be double checked before reinstalling the gun, also there should be no electrical contact between any two pins other than for the filament. Most important, the ceramic base of the filament should be firmly in its seat and held positively in position. A new retaining clip was designed as the original retaining wires did not work well.

After the gun is fitted, but before the flanges are fully tightened, check for a short between pin 5 and the casing. A spring clip on the gun occasionally causes a short. This can also be checked for by plugging in the gun and applying a pedestal voltage. If the correct pedestal voltage can be applied no short exists. As the spectrometer must be baked out after each gun installation it is worthwhile to do the above checks carefully.

Operation and adjustments

The new filament must be outgassed before use, after a bakeout even an old filament may require outgassing. The pressure in the system must be less than 5×10^{-8}, usually it is 1 to 2×10^{-9} torr, valve V16 must be open. To outgas, the filament current is slowly increased (beam energy is OFF, beam current set to the 100 μA range), but maintaining the gun pressure at less that 5×10^{-8} torr. Outgassing may take up to two hours. The beam current should start flowing at about 2.8 - 3A for a new filament, at lower values for an old filament.

Filaments are easily burned out. Refer to Fig. 3.1 for the response of beam current to filament current. Each filament normally has different characteristics, their maximum operating currents must be determined, usually it is approximately 3.2 - 3.4A. Often the beam current is very slow to start, don't attempt to push the filament current up beyond 3.0A. A procedure used was to use acetylene gas as a conditioner for the electrode. The acetylene gas is admitted as a normal sample gas (sec. 3.). After a fifteen minute treatment beam current should be flowing. If the filament has been correctly installed a maximum beam current of 500 - 1000 μA should be obtained. The electron gun power supply has been checked and adjusted to give maximum beam current therefore a low current flow is probably due to the filament being too far away from the anode, ie. it is not properly fitted into its "cup".

The positioning of the electron beam must now be adjusted to allow it to pass through the differential pumping system to the collision chamber. This is done by means of the X, Y position controls. If a filament has been replaced then the positioning of the gun on its base has been altered and new X, Y settings must be found. Acetylene is a convenient gas to use for positioning the beam as the filament can be conditioned at the same time, however any gas for which the energy of a Auger emission peak is known can be used. The procedure is usually time consuming, although with luck it could be done in five minutes. The spectrometer should be turned ON as described in sec. 2.4, then proceed as follows:

- adjust the filament current to approximately 3A to give a maximum beam current of more than 300 μA
- set the beam current on the 100 μA range
- turn the beam energy up to 5 kV
- if acetylene is being used adjust the pedestal supply to

257V. The analyzer energy should be at 50 eV and the slit set at 2mm. The gas pressure should be 2×10^{-7} torr on the gun ionization gauge. The detector is set at 3.2 kV and the E setting at 1/10 full scale. Set the rate meter at the 1×10^4 counts per second range and the time constant at 0.33 seconds.

Unless the beam happens to be properly aligned, then little or no intensity will be indicated on the rate meter. The task is to find the X, Y positions which will give a maximum signal due to Auger current. The problem is that scattered beam electrons give a much larger intensity. The two can be distinguished because the intensity of the scattered peaked is very much greater (over the range of 1×10^4) and because increasing the pedestal voltage by 5V will decrease the Auger current intensity but not the scattered peak intensity. Proceed as follows:

- adjust both the X and Y controls to 5 (assume total range is 0 - 10), and the focus to 10,

- slowly vary the X control while looking for an increase in intensity. If the intensity can be peaked with the X control then similarly peak it with the Y control. Probably the scattered peak has been located. If no peak is found then adjust the Y control to 4 or 6 and repeat the procedure until an increase in intensity is noted.

- to determine if the Auger peak has been located increase the pedestal voltage by 5V, the intensity should drop. If it does not than a scattered peak has been located. The Auger peak should be nearby. Again vary the controls. As the intensity falls look for a small leveling off, or increase, before the intensity falls again. When this is found, probably in the 1×10^4 counts per second range, then adjust X and Y to obtain the peak. Check that it is an Auger peak.

- when the Auger peak is located adjust the pedestal voltage to obtain the maximum intensity. Then adjust X and Y again to obtain maximum intensity.

- the focus control should now be adjusted to give the best signal-to-background ratio. This is conveniently done using the recorder. First set the pedestal to the E_p value then set it to E_b. A vertical line is obtained, the top of which is I_p and the bottom of which is I_b. If the focus is

Electron Beam Inlet

Sight Hole
(behind clip)

Pedestal
Voltage
Feed

Position
Adjusting
Screws

Gas Inlet ———   Ceramic Insert
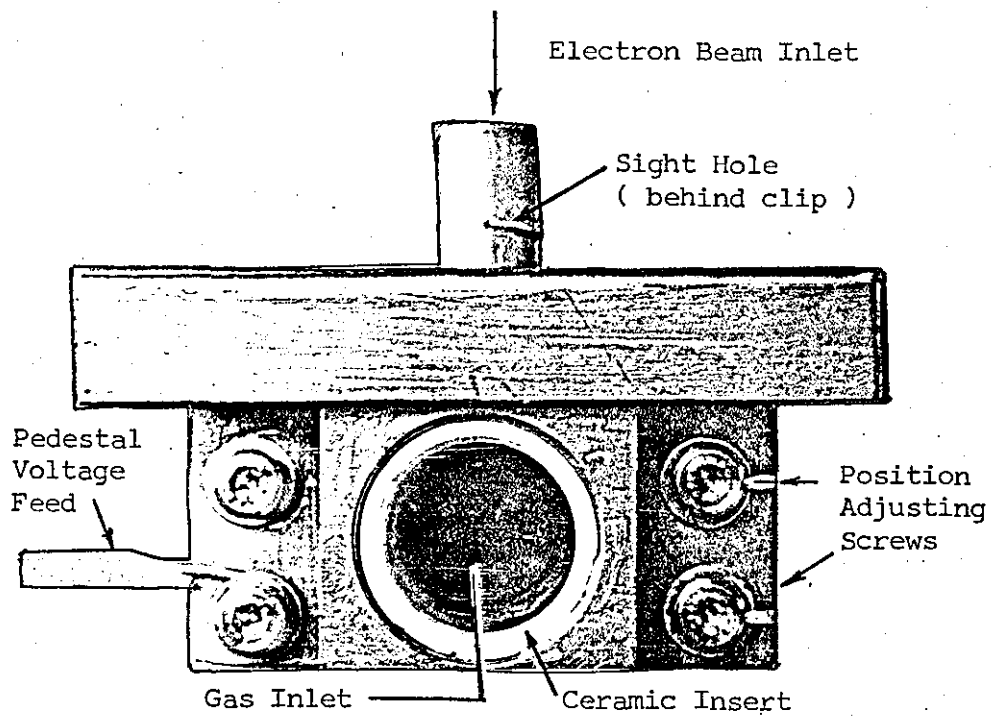
Fig. 2.12.   The gas collision chamber.
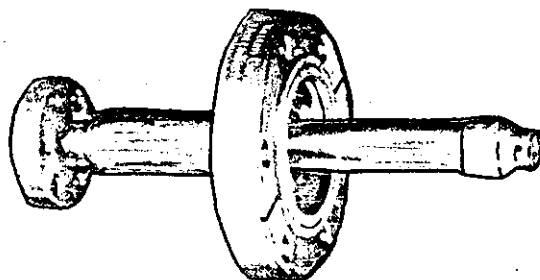
Fig. 2.13.   The gas inlet probe.

simply adjusted for maximum intensity then the best

signal to background ratio may not be obtained (sec. 3.2.5)

Filament current and beam current can be changed without
altering the beam position significantly, however a change in beam
energy requires a readjustment of the X and Y positioning (sec.
3.2.4).

To obtain maximum filament life minimum filament current,
beam current and beam energy should be used. However to obtain the
best instrument performance high values for each of the above are
usually required (sec. 3.2).

2.3.2. The Collision Chamber

The collision chamber or the source volume is the chamber
in which discrete energy Auger electrons are created. The sample
gas (the target) is passed into the chamber (Fig. 2.12) through
the gas inlet probe (Fig. 2.13). The gun electron beam excites
the sample and the Auger electrons leave the chamber to enter the
analyzer through a slit. Before leaving the collision chamber the
electrons are decelerated by means of the pedestal and scan ampli-
tude voltage.

The collision chamber is mounted on the analyzer block (Fig.
2.16). It normally does not have to be adjusted. Fig. 2.14 shows
four detailed views of the chamber.

Three problems have been encountered with the chamber. The
grid over the electron exit hole shorted to the slit plate, the
chamber shorted to the chamber heater, and it shorted to the gas
inlet probe.

The grid was replaced by the manufacturer. Since then only
a momentary short has occured when the slit plate was rotated to
a 0.5 mm. setting. Under the conditions of high potential, loose
wires of the grid arc out to the slit plate. Using only slight
rotation of the plate for settings of 2 and 1 mm. has not resulted
in any reoccurance of this problem. If the problem does reoccur
then the analyzer and chamber will have to be removed. The loose
strands can then either be bent back or preferably cut off with
very small wire cutters.

The short to the chamber heater resulted from "Dag"
(graphite in isopropyl alcohol) on the ceramic insulator of the
heater. This was detected using an Avo meter and checking each
pin in the multipin socket (Fig. 2.15), under the analyzer chamber,
to determine if it was in contact with the pedestal supply pin to

Grid

Slit Plate

Electron Path
Sight Hole

Collision
Chamber

Chamber Mounting
Plate

Electron Path
Sight Hole

Electron
Exit Hole

A

A

A

A

A

$15°$

$15°$

$15°$

$1mm$
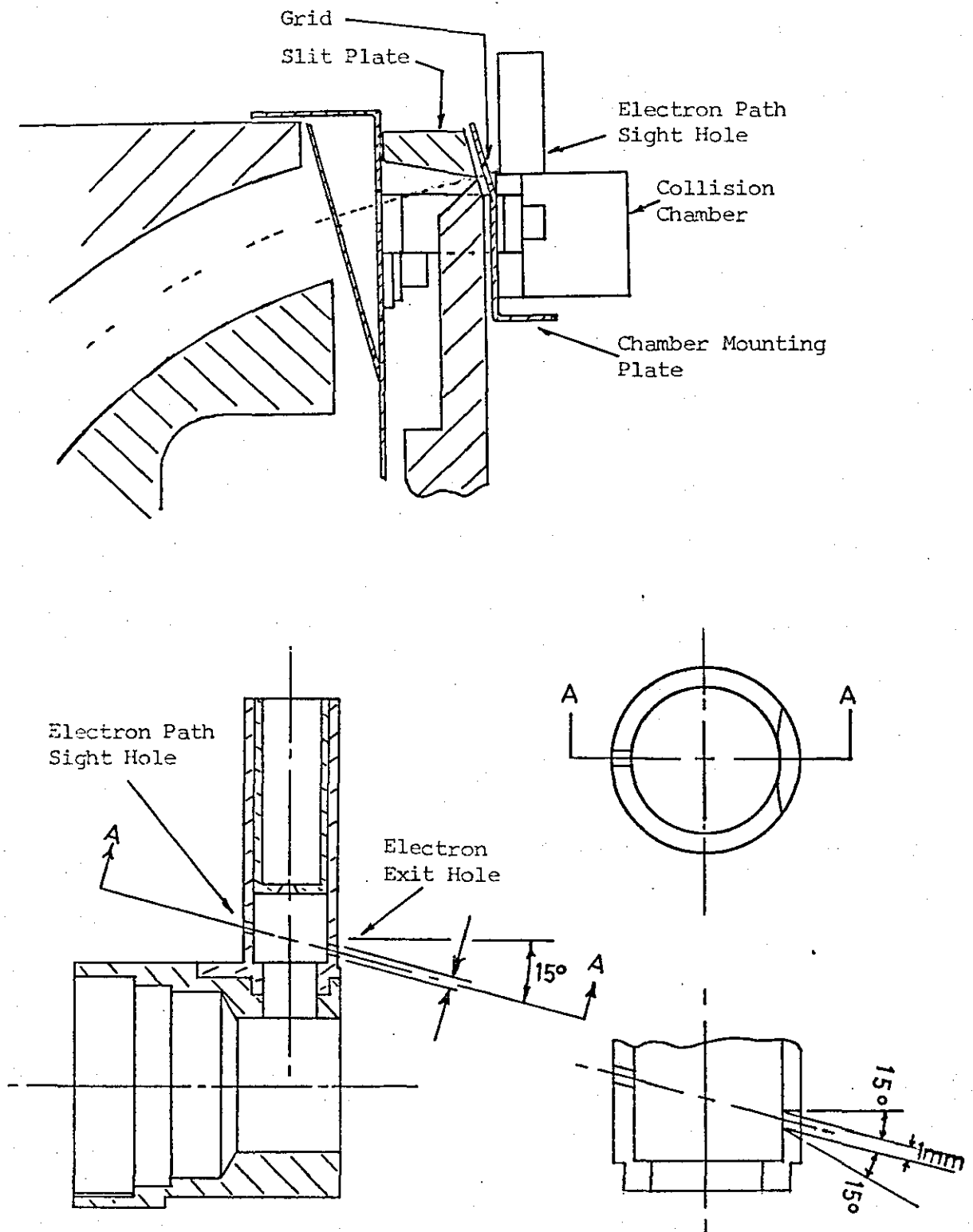
Fig. 2.14. The collision chamber.

the chamber. The ceramic insulator was cleaned in a flame.
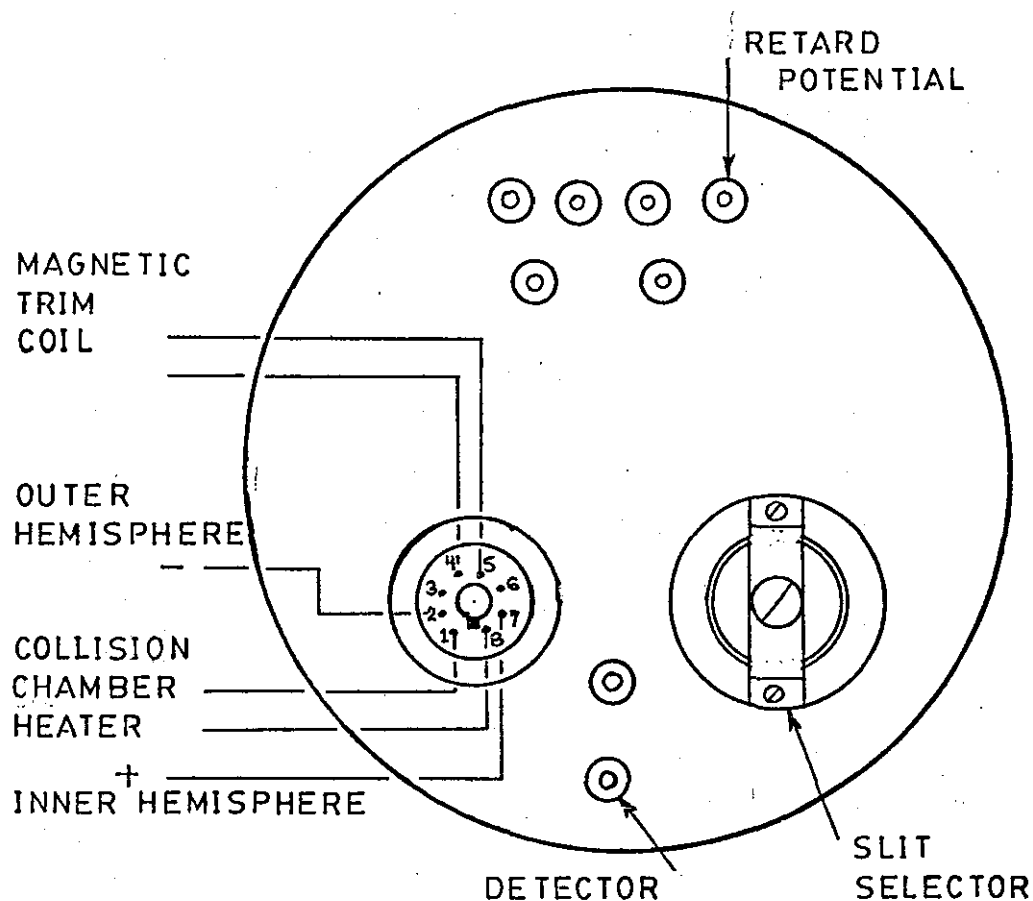
Fig. 2.15. Electrical connections to the spectrometer. (Bottom outside plate of the analyzer flange).

The short between the chamber and gas inlet probe was corrected by replacing the ceramic insulator (Fig. 2.12) and by shortening the gas inlet probe.

If the chamber is removed then it must be realigned after replacement. This procedure is not exact, some design changes would improve the situation. To realign proceed as follows:

- reinstall as shown in Figs. 2.12, 2.14 but just lightly tighten the position adjusting screws.
- remove the wire clip on the tube at the top and slide up the metal cover.
- this exposes the "sight hole". Fig. 2.14 shows how the sight hole, the electron exit hole, the hole in the chamber mounting plate, the slit and the entrance to the analyzer

are aligned. The problem is that a light source cannot be placed in the analyzer, therefore it is difficult to see anything. If the chamber mounting plate was removed it should be centred over the slit before the chamber is mounted.

- the drive-bar to the slit plate can be removed and the plate easily rotated to a horizontal position. By placing a "target" piece of paper over the entrance to the analyzer, illuminating it and then sighting through the sight hole the chamber can be moved until it is roughly aligned with the "target". It is at best an approximate procedure. Replace the slit plate.

- replace the sight-hole cover and wire clip.

- the chamber should be cleaned, particularly the exciting electron entry tube and the Auger electron exit hole. It should also be coated with Dag, however use a minimum amount and then polish the Dag.

- reinsert a clean ceramic insulator. Note that is is threaded.

2.3.3. The Analyzer

The analyzer acts as a narrow pass filter letting through electrons of a narrow energy distribution. It consists of two 150° spherical sections and a slit plate with entrance and exit slits. The electrostatic plates or hemispheres can focus the electrons in two directions with good resolution and without undue loss in intensity. The mean radius of the hemispheres is 10 cm with a gap between them of 2 cm. HV is the energy of the electron passed through the analyzer, where V is the potential difference between the inner and outer hemispheres and H is a constant determined by the physical dimensions, i.e. e=HV. Referring to Figs. 2.14 and 2.8, electrons are retarded to an energy HV by the potential difference between the collision chamber and the electrical centre point of the hemispheres. If K is the electron kinetic energy, R the retarding voltage and W the space charge in the collision zone then K= R+HV+W

In practice the analyzer allows through electrons with an energy range de. This energy range depends on the electron energy, the hemisphere radius, the slit width and the angle of acceptance of the analyzer. A good approximation [4] for a hemispherical analyzer with equal slits is:

Pedestal Feed

Electron Beam Inlet

Magnetic Trim

Collision Chamber
Gas Inlet

Heater Feed

Slit Plate

Analyzer Hemisphere
Plate Feeds

Detector

Slit Control
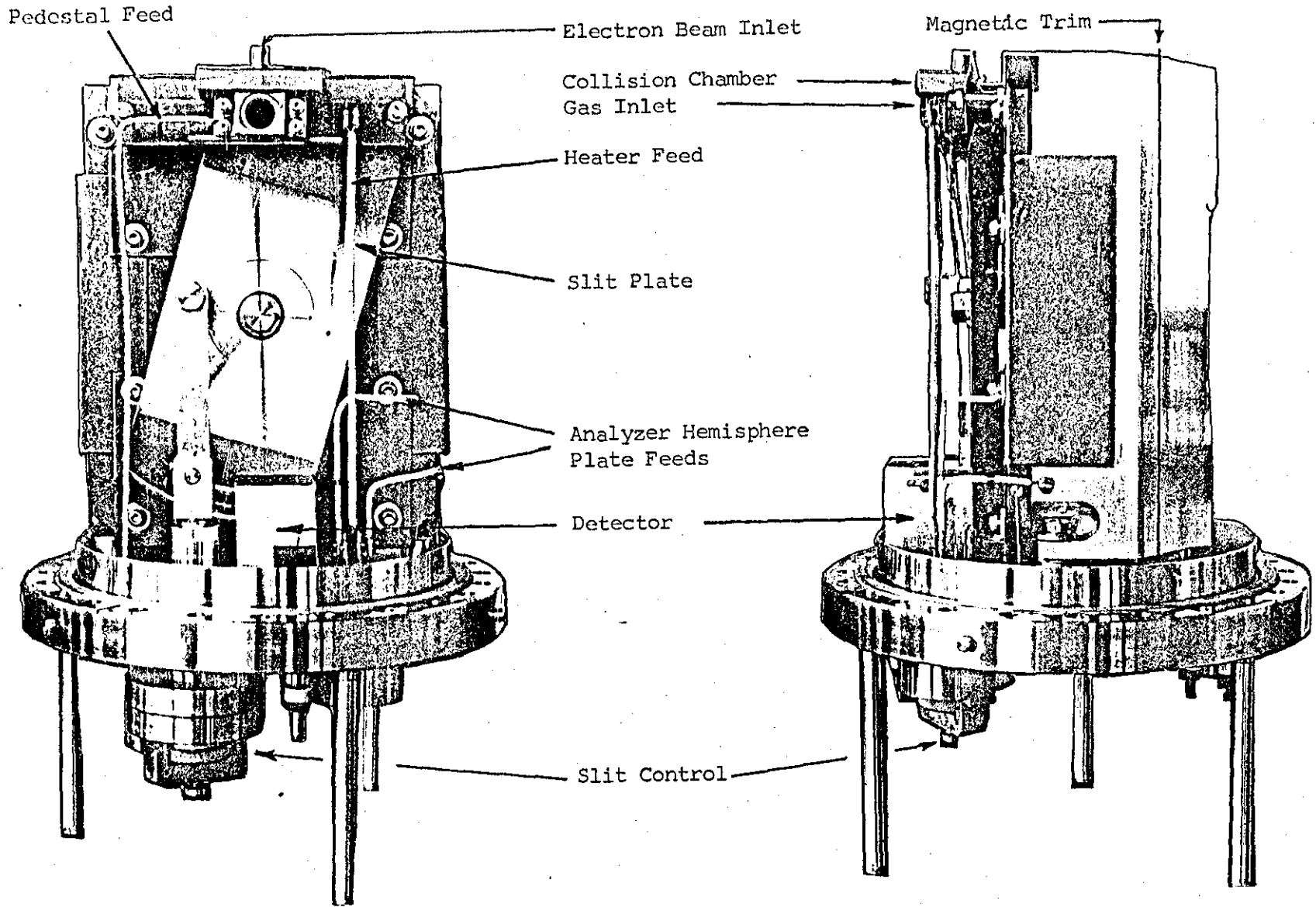
Fig. 2.16. The Auger electron analyzer, the collision chamber and detector.

32

$$\frac{de}{e} = \frac{dr}{2r}$$

where r = mean radius of hemispheres.

dr = slit width

e = energy of electron

de = energy range, full width at half maximum (FWHM)

If the potential applied to the hemispheres (V) is decreased then the energy of the electrons passed is decreased and since de / e is fixed for a certain geometry then de decreases linearly with e. The analyzer resolution thus can be controlled by both the analyzer potential and the slit width, sec. 3.3 discusses these parameters in more detail.

The controls for the analyzer are contained in the spectro-meter control console (Fig. 2.9). The analyzer control unit consists of:

Pedestal Supply — sets the start valve for the retard poten-tial. Its output is variable up to 1500 V. When recording a spectrum this is set to the initial Auger kinetic energy required. When measuring Auger intensity for quantitative analysis the energy of the required Auger peak is set here (Fig. 2.8).

Scan Amplitude — the scan amplitude is adjustable to 1,3,10, 30,100,300 and 1000 V by means of the scan amplitude switch. The scan is begun by setting the start/reset switch to start. Analyzer Energy — this control is for the analyzer supply and allows the selection of analyzing energies of 2,5,10,20, and 50 eV.

Magnetic Trim — was ineffective and therefore not used.

The digital voltmeter measures the retard potential referenced to earth. This arrangement means that

DVM reading = R + HV + W = Auger kinetic energy

The slit plate is mounted on a shaft going through the centre of the hemispheres. It is linked to a linear drive on the base flange (Fig. 2.16). The four slit sizes are $\frac{1}{4}$, $\frac{1}{2}$, 1 and 2 mm. They can be selected by rotating the drivenut on the slit control, the length of the visible thread corresponds to slit widths as follows:

visible length	4 mm	10 mm	17 mm	22 mm
slit width	2 mm	1 mm	$\frac{1}{2}$ mm	$\frac{1}{4}$ mm

The lengths given in the original instrument manual are incorrect.

The only problems associated with the analyzer have been indicated by either an unsteady DVM reading and/or a limited DVM range, much less than its maximum of 1500 V. These have been traced to electrical shorts either in the collision shamber or the electron gun. For further details refer to secs. 2.3.2 and 2.3.1.

2.3.4. The Detector

The detector is a Mullard channel electron multiplier. A channel electron multiplier is a small curved glass tube, the inside wall of which is coated with a resistive material. When a potential is applied between the ends of the tube the resistive surface forms a continuous dynode, analogous to the separate dynodes of a conventional photomultiplier together with its associated resistive chain.

An electron entering the negative potential end of the multiplier generates secondary electrons on collision with the wall of the tube. These are accelerated along the tube until they strike the wall again where they generate further secondary electrons. This avalanching process continues along the length of the tube producing a large pulse of electrons at the positive end of the tube. The multiplier must operate in a vacuum.

A typical gain is 2×10^{8} at an operating voltage of 2.5 kV. The gain however is not constant, it decreases with count rate. Refer to sec. 3.4 for more details. The maximum operating voltage is 3.5 kV, maximum operating temperature is 70°C, maximum ambient pressure with high voltage applied is 3.7×10^{-4} torr.
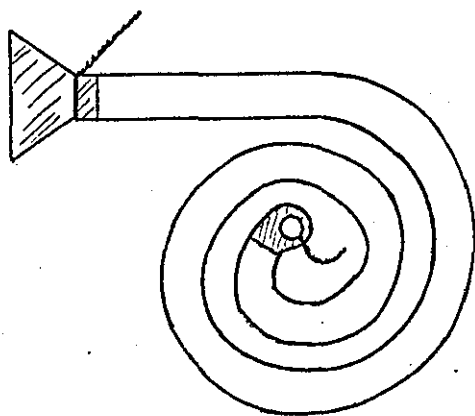
Channel Electron Multiplier

The multiplier is mounted next to the exit slit (Fig. 2.16), it has a protective metal cover. It is very delicate and very expensive. It is sensitive to gases, however no studies were undertaken in this regard.

Pulses from the detector have a duration of about 10^{-9} seconds. The overall dead time of the counting circuit should therefore be quite low. These pulses are then fed to the amplifier which has an adjustable gain, maximum gain was used. From the amplifier they go to an analyzer or low energy discriminator (E control). This control allows through only pulses with an energy greater than E. However as the gain decreases with increasing count rate, E should be decreased at higher count rates. Sec. 3.4 examines this in more detail. It is however a weak point for a quantitative analysis system. The pulses from the discriminator are then converted to 5 V (500 nanoseconds) NIM standard pulses which are then fed to the built-in ratemeter and to the scaler-timer which has been used in these studies. The ratemeter supplies the output for the recorder.

Only the electron multiplier presently in the spectrometer has been used, its condition is unknown. The results obtained may have been degraded because of its condition. The only problems associated with the detector has been its background noise level which included large momentary amplitude increases. The usual operating conditions were a multiplier voltage of 3.2 kV and an E setting of 1/10 full scale.

2.3.5. Output Devices

The output devices of the original spectrometer consisted of the ratemeter and the X-Y recorder. For more quantitative work a scaler-timer has been added. These devices meet the minimum needs for analysis.

The Ratemeter

The ratemeter has ranges of 10, 30, 100, 300, 10^3, 3×10^4, 10^5 and 3×10^5 counts per second. A second control allows selection of time constants from values of 0.033, 0.1, 0.33, 1.0, 3.3, 10, 33, and 100 seconds.

It is used primarily for peaking the X, Y positions of the electron gun and the kinetic energy position of an Auger peak and also as an intensity range switch for the X-Y recorder. The selection of a time constant depends on the spectrometer conditions selected, this is discussed further in sec. 3.4. The zero suppress

and expand range controls are discussed in sec. 2.3.5.

The X-Y Recorder

The recorder is used to record the output of a spectro-meter scan, i.e. to obtain the Auger spectrum. Although it is inexpensive, it is unable to store the data for further processing. Therefore the recorded spectrum is difficult to analyze for real and spurious peaks.

The X axis is connected to the scan amplitude supply; initial and final DVM readings correspond to initial and final energy limits of the recorded spectrum. Unfortunately on recycle the recorder pen doesn't always return to the same starting point. This makes internal standard calibration more necessary if energy positions of several spectra are to be compared (sec. 4.5).

The Y axis is connected to the output of the ratemeter. Two important controls related to the ratemeter and the recorder are the "Zero Suppress" and the "Expand Range". They can be used for both suppressing the zero of the ratemeter output and to expand its range. They are used to expand small peaks on a large background, more details are given in sec. 2.4.

The Scaler-Timer

The scaler-timer is a digital output mode used for quantitative analysis. Pulses from the energy discriminator are counted by the scaler which in turn is coupled to a timer. This allows counting statistics to be applied to the data. Two modes of counting are possible, fixed time and fixed count. Also a digital output of intensity in counts per second is available.

The operation consists of ensuring that the output from the discriminator is plugged into the scaler-timer, switching the unit ON, and then selecting the count time or preset count as desired. No problems were encountered with the unit which was a Nuclear Enter-prises Ltd. SR5 Scaler-Ratemeter.

2.3.6. Removal and Replacement of the Analyzer

Removal of the analyzer is necessary if the slit plate is shorting against the grid of the collision chamber mounting plate (sec. 2.3.2), to replace the detector, or to adjust the collision chamber.

Proceed as follows:

— Close valves V1, V16 and V20.

— let the chamber up to air (sec. 2.2.2).

— VG instructs that the gun and the T piece over the

differential pumping tube should be removed, but this
seems to be unnecessary (an annealed copper gasket is
necessary here).

- Unbolt the flanges between V24 and the sample expansion
  chamber. Then unbolt the flange between the sample inlet
  probe and the analyzer chamber. Rotate the assembly,
  carefully, by 90° and then pull out carefully. The
  ceramic insulator in the collision chamber could be
  broken in this procedure if care is not exercised.

- Unbolt the large flange between the analyzer and the
  chamber. The analyzer will now be supported by the three
  brackets bolted to the chamber flange.

- Screw the three support rods into the appropriate holes
  in the bottom of the flange (Fig. 2.16).

- This operation is best done by two people. Rotate the
  analyzer flange so that it comes out of the brackets (the
  analyzer is heavy); then slide the analyzer downwards while
  carefully maintaining its vertical position.

The analyzer is replaced using the reverse procedure. The
analyzer flange must be tightened up fully, use a procedure similar
to the one suggested in sec. 2.2.3, before the gas probe is inserted.
If the ceramic insulator happens to break it can be removed (screwed
out) and replaced without again removing the analyzer. When the gas
inlet probe is being tightened an AVO meter should be used to ensure
that there is no electrical contact between the probe and the pedestal
supply pin on the bottom flange (Fig. 2.15). Before applying a vacuum
the AVO meter should also be used to check for shorts between the pins
on the bottom of the analyzer and the chamber, this should also be
done before reinstalling the analyzer.

2.4. Operating the Spectrometer

The operating instructions will be illustrated using
acetylene as the sample gas. If another gas is selected check in
appendix C for a spectrum. If one is available then use the con-
ditions listed (if a beam current of 1 μA is listed then use at least
50 μA). It is assumed that the vacuum systems are operating (sec.
2.2) and that the spectrometer is operational. The pressure in the
spectrometer should be less than 10^{-7} torr, the gun trip control
should be set at 10^{-4} torr, and at least the gun ionization gauge
is switched ON.

2.4.1. Preliminary

- Switch on the Digital Voltmeter (DVM). It takes one
  hour to stabilize. Ensure that its on the 1000 V range.
- Switch on the spectrometer control unit. Turn the
  pedestal voltage up stepwise (100 V steps) to 1000 V
  and then down again. If the voltages on the DVM roughly
  corresponds and there is no "tumbling" of the DVM then
  probably no spectrometer shorts exist.
- Switch on the multiplier mains (but not the voltage to
  the detector).
- Switch on the recorder.
- Switch on the scaler-timer.

2.4.2. Sample Handling

Pure gas samples can be prepared either on the external
sample preparation apparatus (sec. 5.5) or the gas can be admitted
directly into the spectrometer gas containers through valves 8, 9
or 10. Preparing the sample externally is usually more convenient,
less gas is used, and as it is in its own container the sample can
be stored for reuse. As acetylene was used frequently, a glass
container of it was connected to inlet valve 8 so it was always
available. Otherwise valves 8, 9 and 10 were little used as the
new sample inlet system (sec. 5.5.3) was much more convenient.
Proceed as follows:

- Attach the sample flask either to V23, or one of V8, 9
  or 10.
- Evacuate the sample chamber (sec. 2.2.2) to a pressure of
  ca. 0.01 torr, then open the valve (V23, 8, 9 or 10) and
  rough out the space between it and the sample container
  valve.
- Close V23 (8, 9 or 10), open the sample valve momentarily,
  close, and then rough out the space again. Close valve 6
  or V21 depending on sample inlet system used.
- Admit the acetylene gas to the sample expansion chamber
  until the pressure on CGS is between 10 and 20 torr.
- Slowly open V24 to admit the gas into the spectrometer.
  Adjust V24 until the gun ionization gauge reads 2×10^{-7}
  torr (do not exceed 5×10^{-7} torr). V24 will have to be
  adjusted frequently to maintain the correct pressure. If
  the pressure in the sample expansion chamber drops below
  5 torr then V24 will have to be closed and then more gas

can be admitted to bring the pressure back to 10 – 20 torr.

2.4.3. Spectrometer Controls

Set the spectrometer controls as follows:

- Analyzer energy to 50 eV.
- Pedestal control to 257.0 (refer to Tables 5.3 and 5.4 for E_p's of other gases).
- Scan amplitude to 100 V.
- Scan time to 300 s.
- Start / Reset to Reset, Polarity to +.
- Slit control to the 2 mm position (sec. 2.3.3).

2.4.4. Pulse Counting Controls and Recorder

Set the controls as follows:

- Gain (rear panel) 1000.
- E control to 10 (range 0 – 10).
- Range, 1×10^4 counts per second.
- Time constant to 0.33 seconds
- Zero suppress to OFF.
- Switch multiplier ON and adjust voltage to 3.2 kV.
- Magnetic trim to minimum value.
- Check that the recorder Y range is 1 V/cm and X range is 2.5 V/cm.
- Place a blank chart paper on the recorder bed and adjust its position to the pen's zero position.

2.4.5. Electron Gun Controls

- Switch ON the power supply.
- Increase the filament current to an appropriate value (sec. 3.2.2). This will be about 3A.
- Set the beam (gun) current to 100 μA. The meter should indicate 100 μA (sec. 3.2.3).
- Switch on the beam (gun) energy and set at 5 kV.

If the X–Y controls of the gun had been previously adjusted then only slight readjustments will be necessary, otherwise refer to sec. 2.3.1.

- Note the intensity reading on the ratemeter. If it is off scale turn it to the next higher range.
- Adjust X and Y slightly until a maximum intensity reading is obtained. Adjust the pedestal voltage again until a maximum intensity is obtained. Readjust X and Y as before.
- Adjust the focus control to obtain the maximum signal-to-

background ratio, refer to section 3.2.2, 10 is a usual setting.

- Ensure that the recorder paper is in place and that the pen rests on the chart zero point when the recorder X and Y inputs are switched OFF.
- Switch X and Y inputs ON.
- Adjust the ratemeter range until the recorder pen is within the chart paper range.
- Check recorder pen switch is set to remote.

2.4.6. <u>Recording a Spectrum</u>

- Adjust sample gas pressure to 2×10^{-7} torr.

The spectrometer could now be used to measure the intensity of the Auger peak of acetylene. If such measurements were required then the scaler-timer could be used (sec. 2.3.5). To make measurements of other Auger peaks or the background, adjust the pedestal voltage to the appropriate energy value (sec. 5.6).

- Adjust pedestal voltage to 200 V (correct for the DVM zero which drifts). This is the starting energy of the carbon spectrum.
- Set the Start/Reset switch to start.

A spectrum should now be recorded showing the Auger peaks. To maximize the quality of the spectrum refer to sec. 3.0 which discusses the operational parameters.

Chapter 3

OPERATIONAL PARAMETERS

3.1. Introduction

This chapter presents the results of an experimental examination of the operational parameters of the AFM2 Auger electron spectrometer. The parameters examined are those of the electron gun excitation source, the Auger electron analyzer, the detector, and the sample introduction system. The time constant and sweep time are also considered.

Both the theoretical and experimental response of changes in each parameter are discussed. As both qualitative and quantitative analysis are of interest in this study two indicaters of performance are considered. The signal-to-background ratio (sec. 5.2.2) indicates those conditions best for qualitative analysis. The figure of merit (sec. 5.4) indicates those conditions best for quantitative analysis.

Some of these parameters were examined in a previous study[1] done at Loughborough. The results presented here expand on this study. They are also more quantitative and are presented in more detail to make them of greater use in selecting the best instrumental conditions of analysis.

3.2. The Electron Gun

3.2.1. General

The parameters of the electron gun include the filament current and the electron beam current, energy, position, and focus.

The parameters of the electron gun are the most difficult to quantify as the response to a certain setting of a parameter depends on the condition of the electron gun filament. Even new filaments do not give the same response for a given value of a parameter. As a filament ages, and depending on the sample gases used, its properties vary and cannot be accurately predicted. An indicator of the filament condition is the maximum electron beam current the gun can supply. The Auger peak intensity (at a fixed beam current) decreases as the maximum possible beam current decreases.

Because of the differences between filaments and the changes they undergo the graphs in this chapter are only indicative of changes in response.

Fig. 3.1. The effects of electron gun filament current. Acetylene, at (gun) gas pressure of 2 X 10^{-7} torr, excited by an electron beam of 3.8 kV and 50 μA. Peak intensity measurements were made at 256.6 eV and background measurements at 266.4 eV. The analyzer was set at 50 eV and the slit width at 2 mm. The detector voltage was 3.2 kV with an E setting of 100/1000. Maximum peak intensity was ca. 6000 counts s^{-1}.

3.2.2. Filament Current

Wooliscroft [1] states that the filament current controls the temperature of the filament and hence the number of electrons emitted by it. An increase in current results in a denser cloud of electrons about the filament and this allows a narrower beam of electrons and a lower background due to less electron scattering.

The gases used in this study of the effect of filament current included acetylene, nitrogen and argon. In addition the effect of other gases on the filament were noted.

The filament current affects the signal-to-background ratio, the figure of merit, and the peak and net intensities of a measurement. It also affects the total primary electron beam current that the electron gun is capable of producing. At a low filament current no electron beam current is produced. As the filament current is increased, a current is reached at which the electron beam current begins. The beam current then increases sharply with increasing filament current until a plateau is reached. As can be seen from Fig. 3.1 the figure of merit and the net signal undergo a similar but sharper increase with filament current. As the filament ages the plateau value of beam current (indicated as maximum gun current on the recorded spectra, Appendix C) decreases. Thus the beam current is used as a guide to the condition of the filament. The filaments used in this study were operated at a current setting on the plateau of maximum beam current.

Changes in filament current did not seem to affect the X, Y positioning of the beam, however these positions should normally be peaked before an analysis.

It was noted that acetylene increased the emission current for a given filament current. This was considered to be due to the production of a pyrolytic graphite coating on the filament. All filaments used in this study were treated with acetylene.

3.2.3. Beam Current

The gases used in this study of the effects of beam current included nitrogen, argon and acetylene. Results obtained were similar but not identical for either the different gases or for the different electrodes used.

The Auger current is expected to be directly proportional to the exciting beam current. [3] The experimentally determined peak and net signal intensities were proportional to the beam current only up to a current of 50 to 100 μA. Higher beam currents caused only
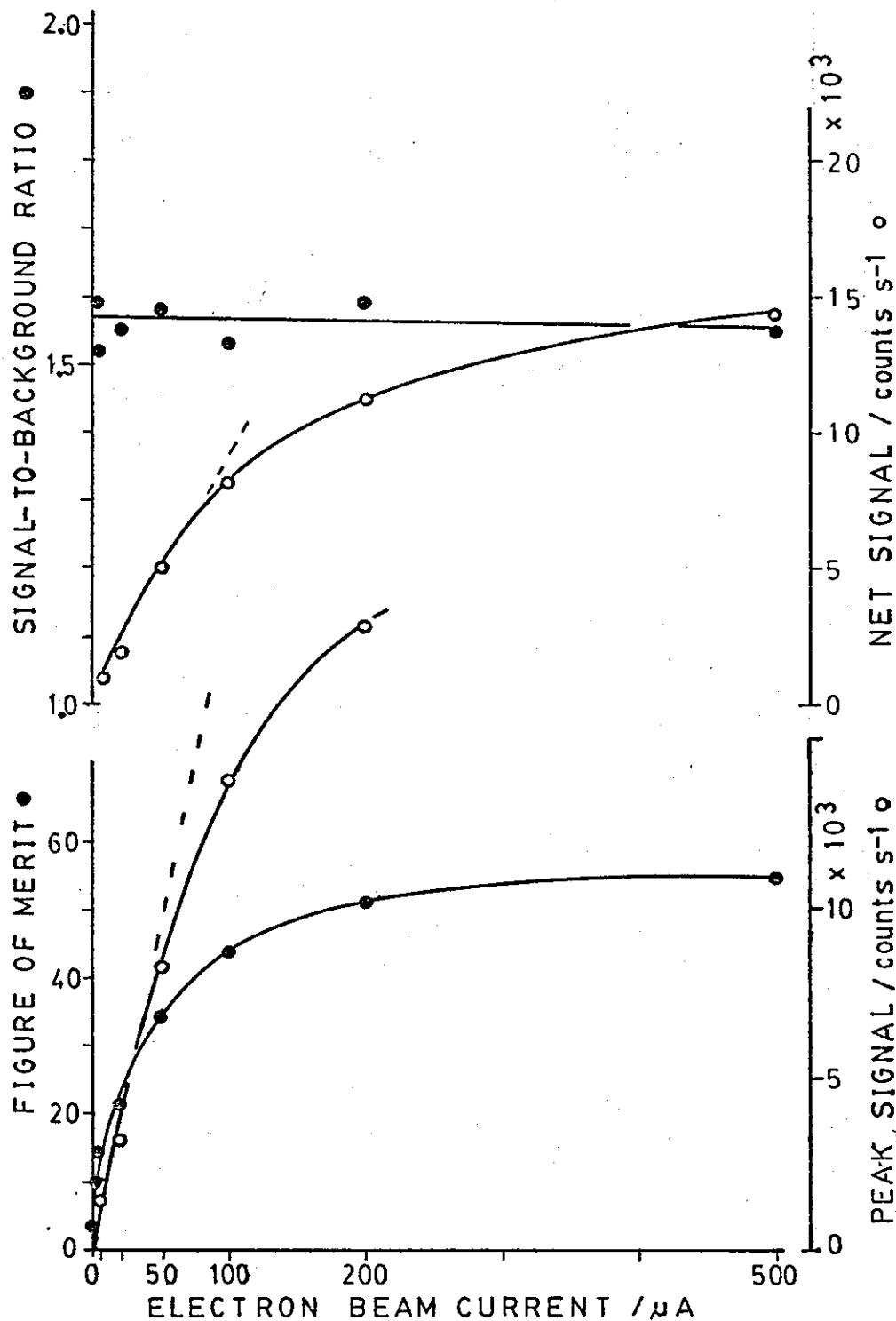
Fig. 3.2. The effects of electron gun beam current. Acetylene, at a (gun) gas pressure of 2×10^{-7} torr, excited by an electron beam of 3.8 kV. Filament current was 3.4 A. Peak intensity measurements were made at 256.6 eV and background measurements at 266.4 eV. The analyzer was set at 50 eV and the slit width at 2 mm. The detector voltage was 3.2 kV with an E setting of 100/ 1000. Maximum peak intensity was ca. 23,000 counts s^{-1}.

slightly higher signal intensities.

Signal-to-background ratios were generally slightly higher at low beam currents (ca. 10 - 100 μA) and tended to decrease with increasing beam current.

The value of the figure of merit initially increased sharply with increasing beam current. Increasingly higher beam currents however only caused small increases.

The effects of beam current when acetylene was examined is illustrated in Fig. 3.2.

3.2.4. Beam Energy

Wooliscroft[1] has reviewed the literature in regards to the effect of electron beam energy on the Auger current. It is expected that from a consideration of ionization cross-section variation and backscattering that maximum peak intensities might occur in the region of 3 to 6 times the critical ionization potential. Pessa[2] calculated the optimum source energy to be about 5 keV. This seems to be the most used energy for gas studies.

The experimental results obtained by Wooliscroft indicated the optimum source energy to be in the region of 4.7 - 5.0 keV. His study included argon, ammonia, hydrogen sulfide, and hydrogen chloride. This study produced similar results for nitrogen and acetylene however the signal-to-background variation with source energy was different. Wooliscroft's curves showed a definite peak in the signal-to background ratio vs. beam energy. The results of this study (Fig. 3.3) however, showed a leveling off of the ratio or a slight decrease after the maximum ratio had been obtained. Wooliscroft's data resemble the curves obtained in this study when the X, Y position of the beam was not maximized after each change in beam energy. Changes in beam energy have a definite effect on the X, Y position of the electron beam (Table 3.1).

Fig. 3.3 indicates the variation of signal-to-background ratio, figure of merit and net Auger intensity for acetylene. Other data obtained showed less or no decrease in the variables with electron beam energy and indicated that 5 keV (the maximum beam energy available) gave maximum values for signal-to-background, figure of merit, and net signal intensity.

3.2.5. X, Y Position of the Electron Beam

Sec. 2.3.1. indicated the need to adjust the position of the electron beam to allow it to pass through the differential pumping system. Changing the electron gun filament current or beam current has little or no effect on the beam position. However, a change in
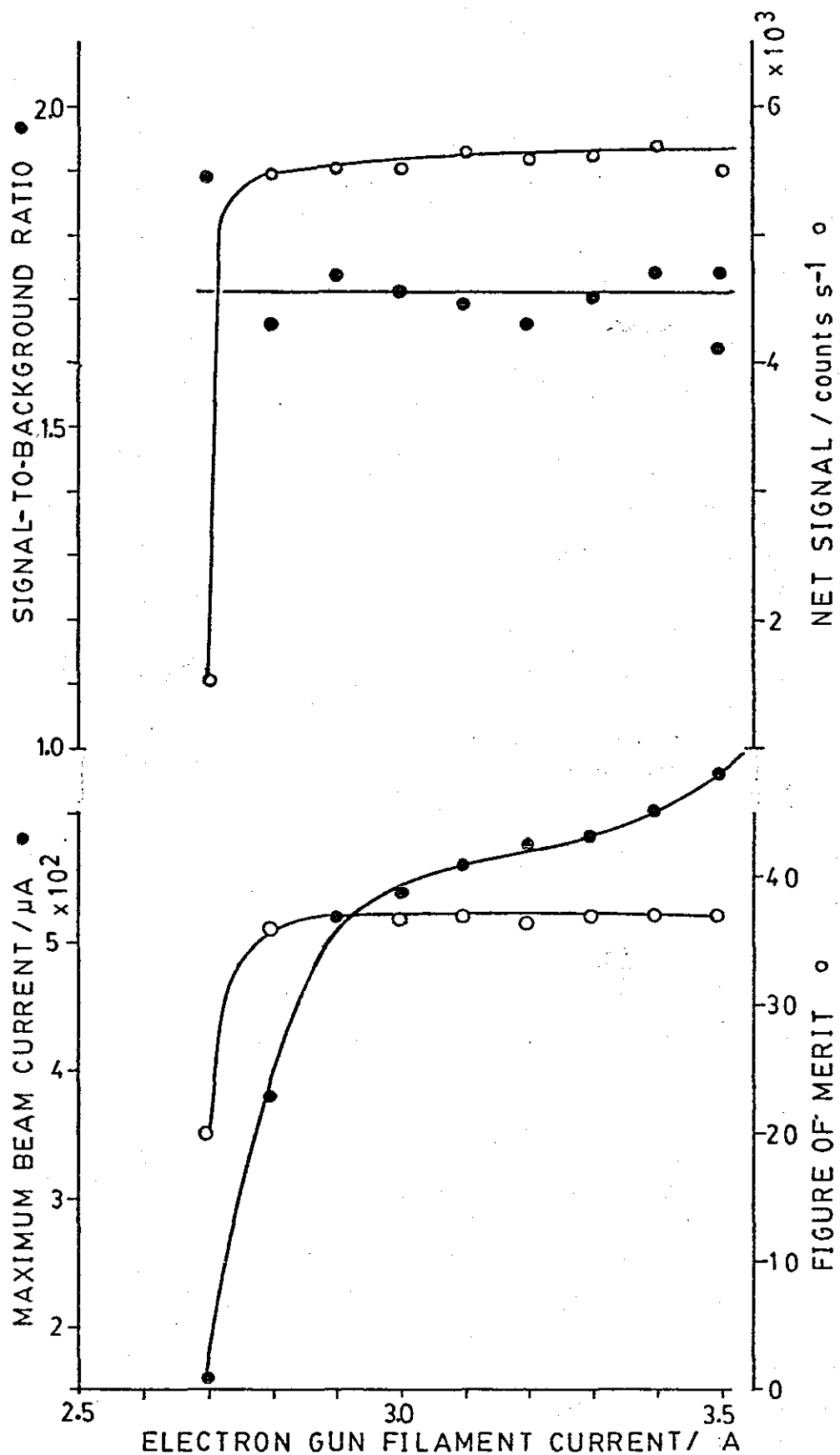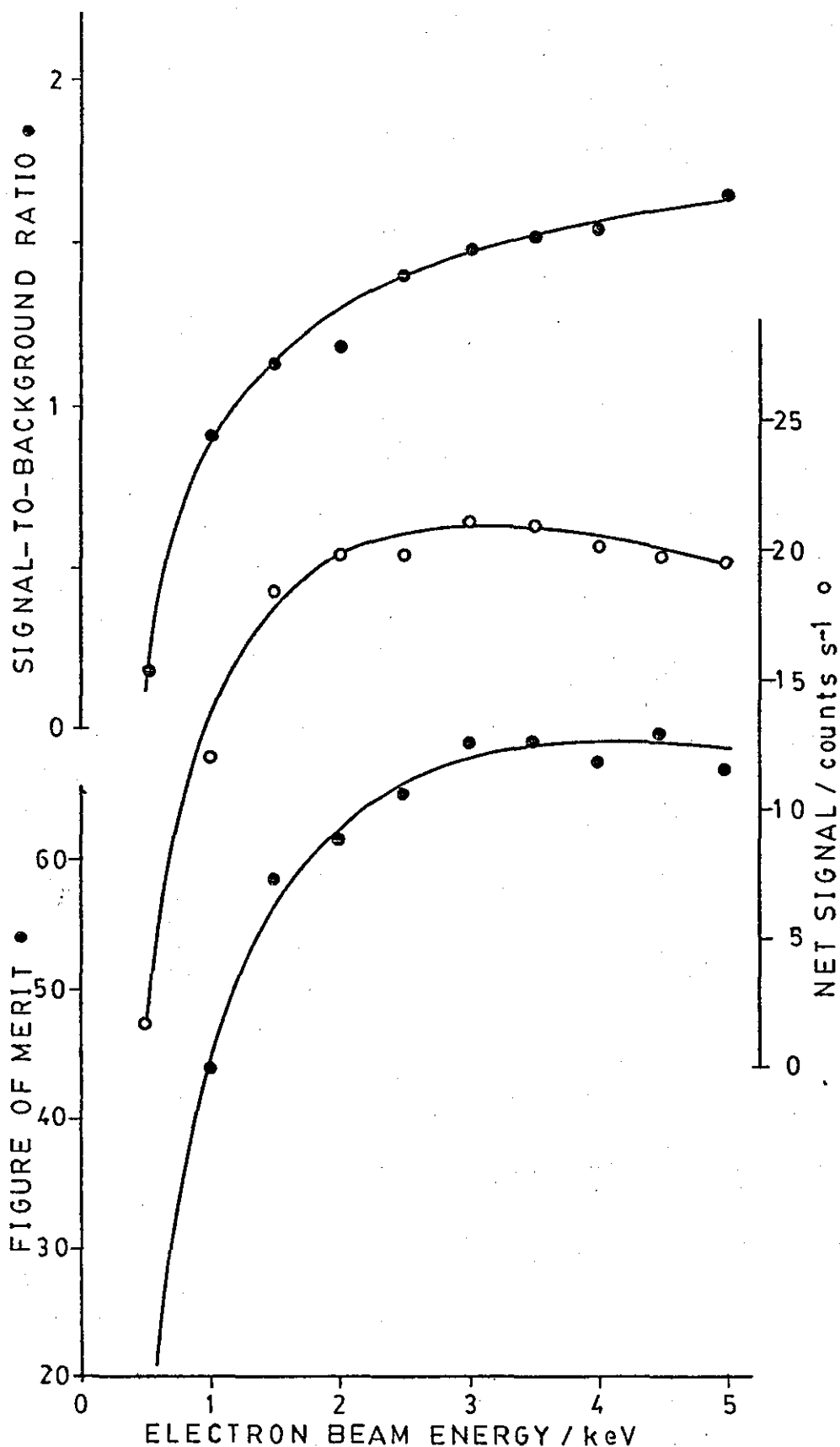
Fig. 3.3. The effects of electron gun beam energy. Acetylene, at a (gun) gas pressure of 2 X 10^{-7} torr, excited by an electron beam of 200 μA. Filament current was 3.4 A. Peak intensity measurements were made at 256.6 eV and background measurements at 266.4 eV. The analyzer was set at 50 eV and the slit width at 2 mm. The detector voltage was 3.2 kV with an E setting of 100/1000. Maximum peak intensity was ca. 31,000 counts s^{-1}.

beam energy has a definite effect on the beam's position. The X
and Y beam position controls must be readjusted to give maximum
Auger signal after any change in beam energy.

The following data indicates the adjustment of the X and Y
controls necessary for different energy settings.

TABLE 3.1

VARIATION OF X AND Y POSITIONS

WITH CHANGES IN ELECTRON BEAM ENERGY

Beam Energy (keV)	1	2	3	4	5
X Position	4.83	4.42	4.15	3.81	3.45
Y Position	5.26	5.60	5.82	6.18	6.40

3.2.6. Beam Focusing

Focusing affects the signal and background count rates and
hence the signal-to-background ratio, figure of merit and net signal.
The effect of focus is indicated by the following table

TABLE 3.2

EFFECTS OF VARIATION OF FOCUS SETTING

Focus Setting	Peak Intensity$_1$ counts s	Background Intensity$_1$ counts s	Signal-to-Background Ratio	Figure of Merit	Net Intensity$_1$ counts s
0	8,200	7,600	0.1	1.1	600
6	11,700	9,400	0.3	3.6	2,300
8	10,900	8,200	0.3	4.4	2,700
9	5,600	3,300	0.7	5.5	2,300
10	2,800	1,400	1.0	4.9	1,400

As the data indicates the focus should be adjusted for best
signal-to-background ratio and not the highest Auger intensity. A
value of 10 usually gave the best signal-to-background ratio.

3.3. The Auger Electron Analyzer

3.3.1. General

The parameters of the electron analyzer include the pedestal
voltage, the analyzer voltage and the slit width. The analyzer is
described in sec. 2.3.3.

The pedestal voltage determines the energy of the Auger
electron which will be detected. The analyzer voltage and the slit
size affects the resolution and sensitivity of the spectrometer.

It is these two parameters which were examined.

3.3.2. Analyzer Voltage

The energy range of electrons passed by the analyzer is affected by the analyzer voltage (sec. 2.3.3.) as follows:

Since $de = e \dfrac{dr}{2r}$

and $e = H V$

where dr = slit width

r = mean radius of analyzer

e = energy of electron

de = energy range (ca. FWHM)

H = instrument constant

V = voltage applied to the analyzer

therefore, if dr and r are constant then $de \propto V$

i.e. de is proportional to the analyzer voltage. Table 3.3 lists calculated energy ranges (de = analyzer voltage x 2 mm / 2 X 100 mm) and experimentally determined FWHMs for the argon 203.47 eV peak. It is seen from this table that the experimentally determined FWHMs are slightly greater than the calculated energy ranges. The FWHM does initially decrease with analyzer voltage as expected; at lower analyzer voltages the FWHM is constant, but this too is as expected.[3]

TABLE 3.3

VARIATION OF ANALYZER RESOLUTION
WITH ANALYZER VOLTAGE

Analyzer Voltage	V	50	20	10	5	2
de (calculated)	eV	0.50	0.20	0.10	0.05	0.02
FWHM (experimental)	eV	0.78	0.49	0.29	0.29	0.29

The sensitivity is approximately proportional to e^2 / K, where K is the energy of the Auger electron. Therefore lower analyzer energies, although giving higher resolution, give lower sensitivities. Table 3.4 lists calculated sensitivities and net signals (normalized to 12.3 for an analyzer voltage of 50 V) for argon (203.47 eV peak). The experimentally determined net signal intensities roughly agree with the calculated sensitivities.

TABLE 3.4

VARIATION OF ANALYZER SENSITIVITY
WITH ANALYZER VOLTAGE

Analyzer Voltage V	50	20	10	5	2
e^2 / K	12.3	2.0	0.5	0.12	0.02
Net Signal	12.3	3.6	1.6	0.4	0.05

The variation of analyzer resolution and sensitivity can be seen graphically in Fig. 3.4. The resolution of the argon peaks at 205.21 and 205.62 eV can be seen to improve with decreasing analyzer voltage, but at the expense of sensitivity.

3.3.3. Slit Width

As the previous section indicated, the energy range of electrons passed by the analyzer are affected by both the analyzer energy and the slit width.

$$de = e \ X \ \frac{dr}{2r}$$

If both e and r are fixed then

$$de \propto dr$$

Table 3.5 lists calculated energy ranges (de = 50 eV / 200 mm X dr) and experimentally determined FWHMs for the argon 203.47 eV peak. The experimentally determined FWHMs are again greater than the calculated energy ranges (sec. 3.2.2). They initially decrease with slit width but again reach a limiting value. The sensitivity is seen to be roughly proportional to the slit width.

TABLE 3.5

VARIATION OF ANALYZER SENSITIVITY AND
RESOLUTION WITH SLIT WIDTH

Slit Width	mm	2	1	$\frac{1}{2}$	$\frac{1}{4}$
de (Calculated)	eV	0.50	0.25	0.125	0.0625
FWHM (experimental)	eV	0.80	0.44	0.31	0.31
Net Signal, normalized		1.00	0.55	0.19	0.10

The variation of analyzer resolution and sensitivity can be seen graphically in Fig. 3.5. The resolution of the argon peaks at 205.21 and 205.62 eV can be seen to improve with decreasing slit width, but at the expense of sensitivity.

Fig. 3.4. The variation of analyzer resolution and sensitivity with analyzer voltage.

50 eV

20 eV

X 3.3

10 eV

X 3.3

203.47 eV

205.21 eV

205.62 eV

X 10

5 eV

X 10

2 eV

1 eV = 0.69 cm
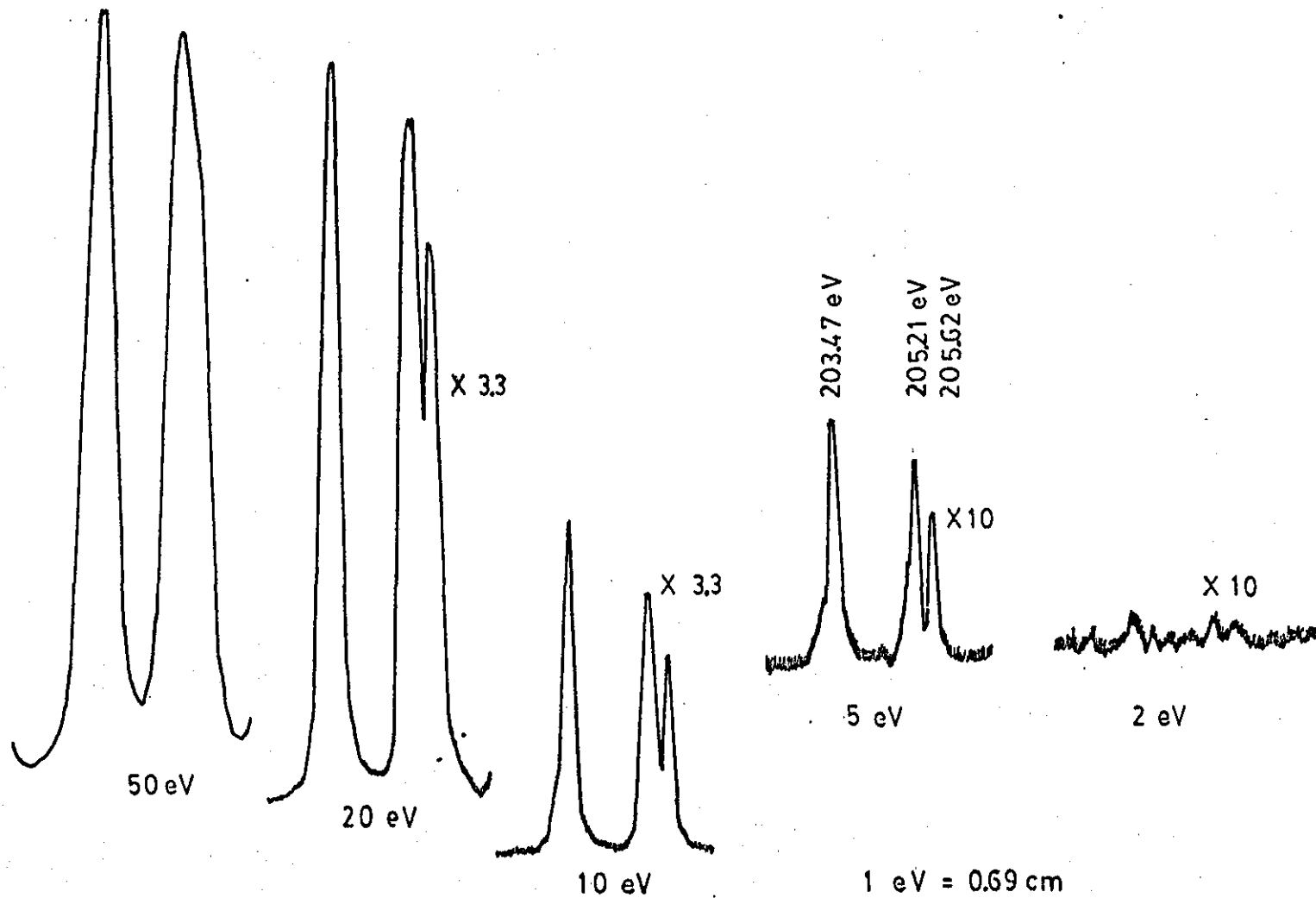
Date 7/20/78
Spectrum No. 1
Sample
    Argon

    sam   20   t
Press ana   t
    gun 1×10^{-7} t

ENERGY SOURCE
Fil curr   3.1   A
Gun curr 200   µA
Voltage   5.0   kV
X 5.45 Y 3.30 F 10
Max fil curr 400µA

ANALYZER
Energy Var.   V
Slits   2   mm

SCAN
Pedestal   V
Amplitude 30   V
Time   300   s
Counts 1×10^5 s^{-1}
T.C.   0.33   s
Zero supp off
Exp x   1

DETECTOR
Mult   3.2   kV
E Set   100/1000
Mag trim   —   mA

Fig. 3.5. The variation of analyzer resolution and sensitivity with slit width.

2 mm

1 mm

1/2 mm

X 3.3

X 10

1/4 mm

1 eV = 0.69 cm

Date   7/20/78
Spectrum No. 2
Sample

Argon

        sam   20   t
Press ana   t
        gun   1×10⁻⁷   t

ENERGY SOURCE
Fil curr   3.1   A
Gun curr   200   µA
Voltage   5.0   kV
X 5.45 y 3.30 F   10
    Max. fil curr 400µA.
ANALYZER
Energy   50   V
Slits   Variable   mm

SCAN
Pedestal   V
Amplitude   30   V
Time   300   s
Counts   1×10⁵   s⁻¹
T.C.   0.33   s
Zero supp   off
Exp x 1

DETECTOR
Mult   3.2   kV
E Set   100/1000
Mag trim   —   mA

51
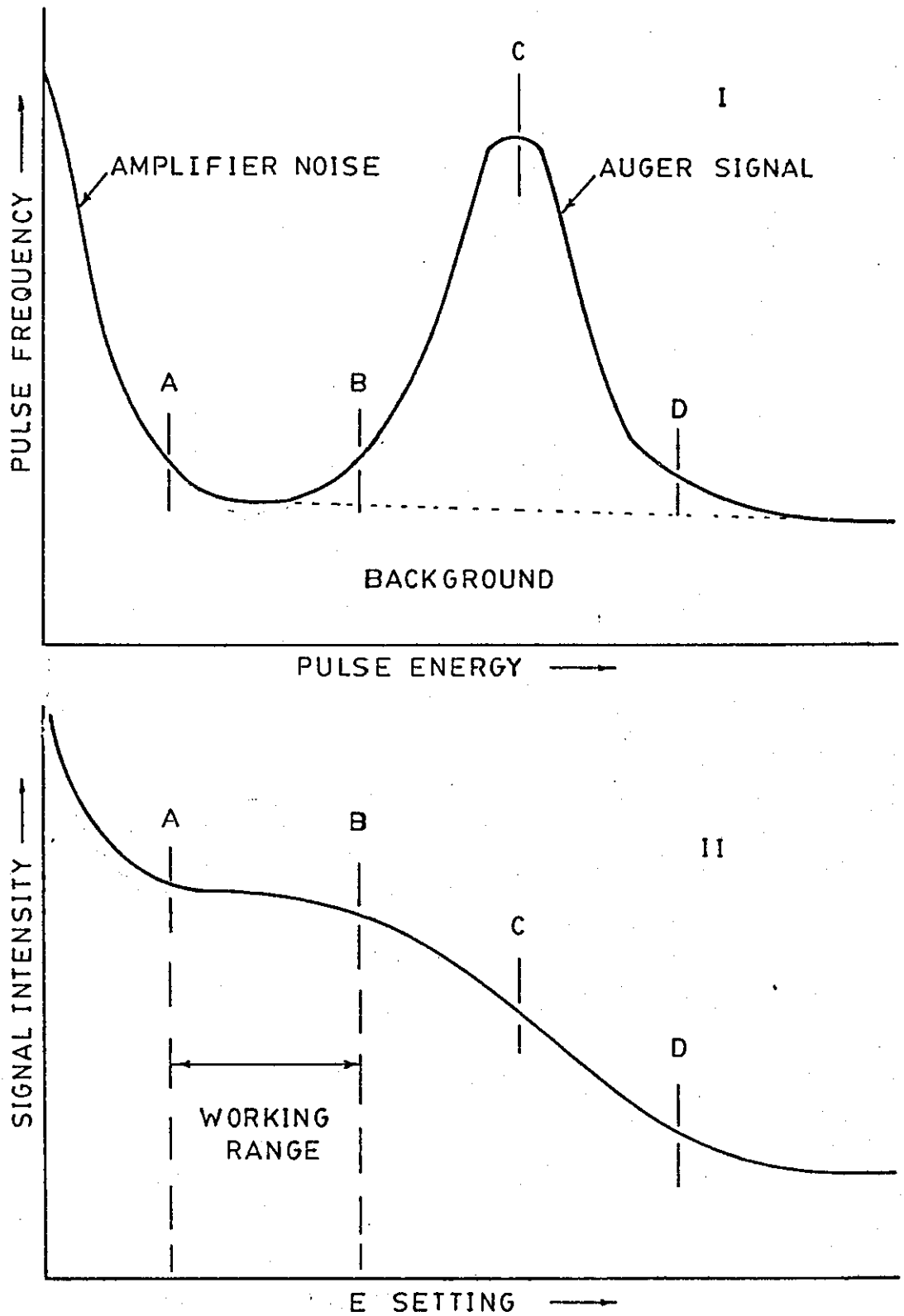
Fig. 3.6. Pulse height selection.
I   Differential pulse height distribution curve.
II Integral pulse height distribution curve.

3.4   The Detector

3.4.1. General

The detector, a channel electron multiplier, is discussed in sec. 2.3.4. This section examines the parameters of detector voltage and E setting of the low energy discriminator.

The pulses produced by the detector contain up to 10^8 electrons, have a duration of about 10 nanoseconds, and have a Gaussian distribution because of their statistical nature of production. The pulses are fed to an amplifier and then to an analyzer (E control). The analyzer lets through only pulses which have an amplitude (pulse height) greater than E. These pulses are then converted to a NIM standard pulse of 5 volts amplitude, and 500 nanoseconds duration before going to the ratemeter and the digital scaler-timer.

A possible distribution of pulses is shown in Fig. 3.6. Also shown is the variation of output signal intensity for this distribution when the E setting is varied. As can be seen, the shape of the initial pulse distribution can be deduced from this second curve. This is what has been attempted in this study.

The "correct" adjustment of the pulse counting controls requires the E setting to be set to a value just lower than the lowest energy of the Auger pulse distribution. In Fig. 3.6 this is between A and B. Also the electron multiplier voltage must be set such that it is on the plateau of the peak intensity vs. detector voltage curve (Fig. 3.9).

A complicating factor is that the gain of the detector varies with Auger current intensity, i.e. at high count rates the average pulse height falls. This requires a lowering of the E setting.

It was thought that a higher signal-to-background and figure of merit might result if the pulse distribution could be isolated by two E settings, i.e. by using a pulse height selector with the lower level set at B and the higher level set at D (Fig. 3.6). In this way only the pulses between B and D would be counted. Therefore only the background beneath the pulse distribution would be counted and hence a lower background would result. This idea was checked by subtracting the counts obtained with E set at B from those obtained when E is set at D (sec. 3.4.2.).
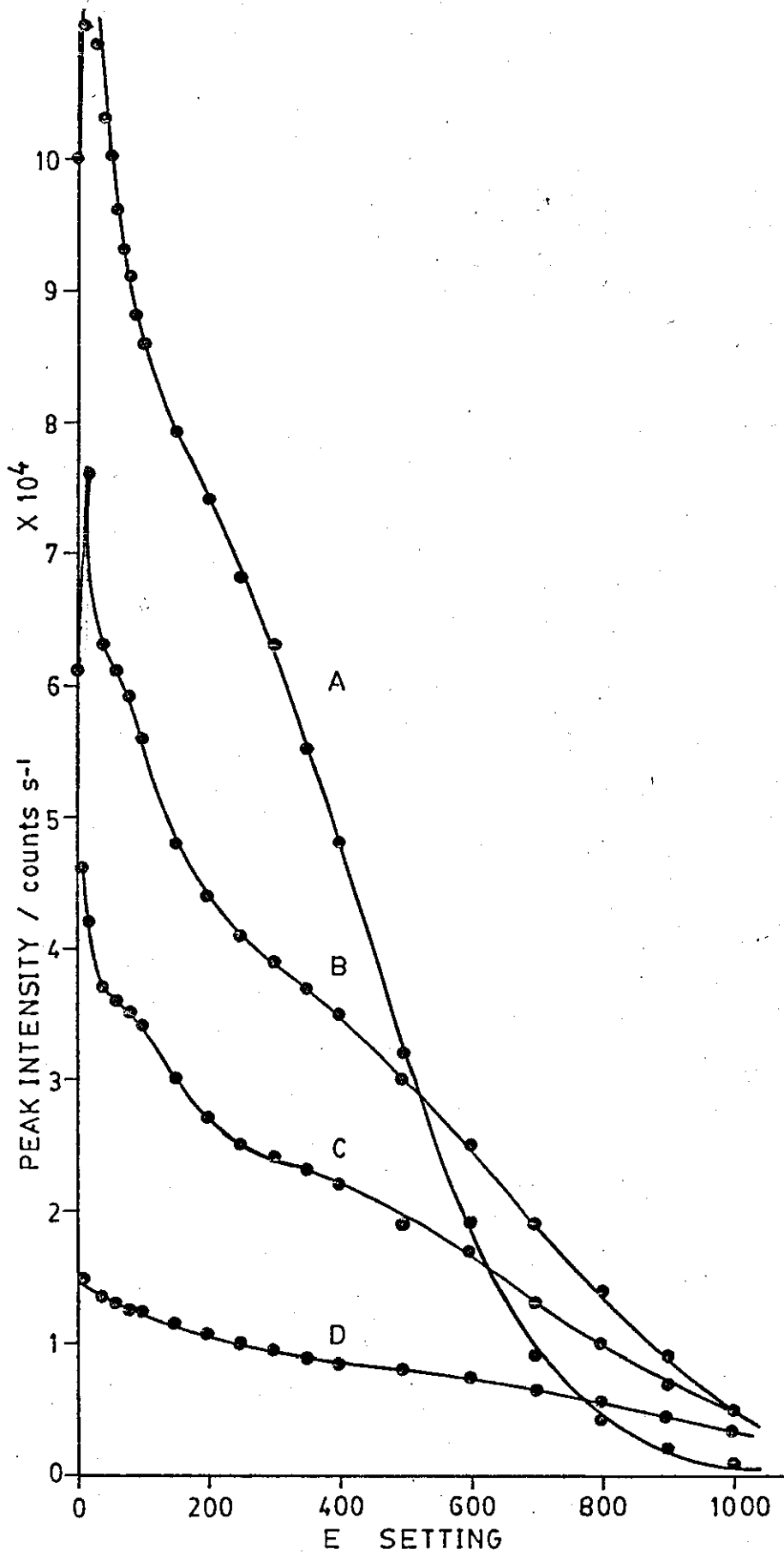
Fig. 3.7. Peak signal intensity as a function of E setting and Auger current. (A: 85 X 10³, B: 50 X 10³, C: 30 X 10³, D: 12 X 10³ counts per second)

3.4.2. E Setting

Fig. 3.7 shows the variation of peak intensity with E setting for four different intensity settings.

Curve A is different from B, C, and D due to strong peak inversion. Peak inversion is illustrated in Fig. 3.8 and will be discussed later in this section. Curves B, C, and D are similar, these were analyzed to determine the original pulse distribution. Unfortunately they were not as expected (Fig. 3.6). Both B and C illustrate the amplifier noise and external interference. The Auger pulse peak maximum appears to be at approximately 150 (E), and the beginning and end of the pulse distribution at approximately 60 and 250 (E). However the beginning and end of the pulse distribution and the tail of the curve do not allow for very exact interpretation. The possibility of a second and larger pulse is suggested by the tail of the curve, however this could be do to peak inversion.

The following table illustrates the possible use of a pulse height selector for reducing signal background.

TABLE 3.6

USE OF A PULSE HEIGHT SELECTOR
FOR REDUCING BACKGROUND SIGNAL

E Setting	CURVE B				CURVE C			
	I_p	I_b	S/B	FM	I_p	I_b	S/B	FM
60	60,839	7,165	7.5	162	35,737	4,991	6.2	118
250	41,222	5,595	6.4	128	24,952	3,927	5.4	95
$I_p - I_p$	19,617		S/B	FM	10,785		S/B	FM
$I_b - I_b$		1,570	11.5	100		1,065	9.1	71

As can be seen from Table 3.6 this technique could possibly be used to reduce background and hence increase the signal-to-background ratio. The value of the figure of merit (FM) however is reduced. If the beginning and the end of the pulse distribution was better known and more defined the technique might be more effective.

The peak inversion which was referred to earlier in this section is illustrated in Fig. 3.8. It is thought that this phenomena is caused by the shifting of the maximum pulse energy (height) to lower values by an increase in the intensity of the Auger signal. The figure illustrates an increasing degree of inversion with

Fig. 3.8. Peak intensity as a function of the E setting.

E SETTING
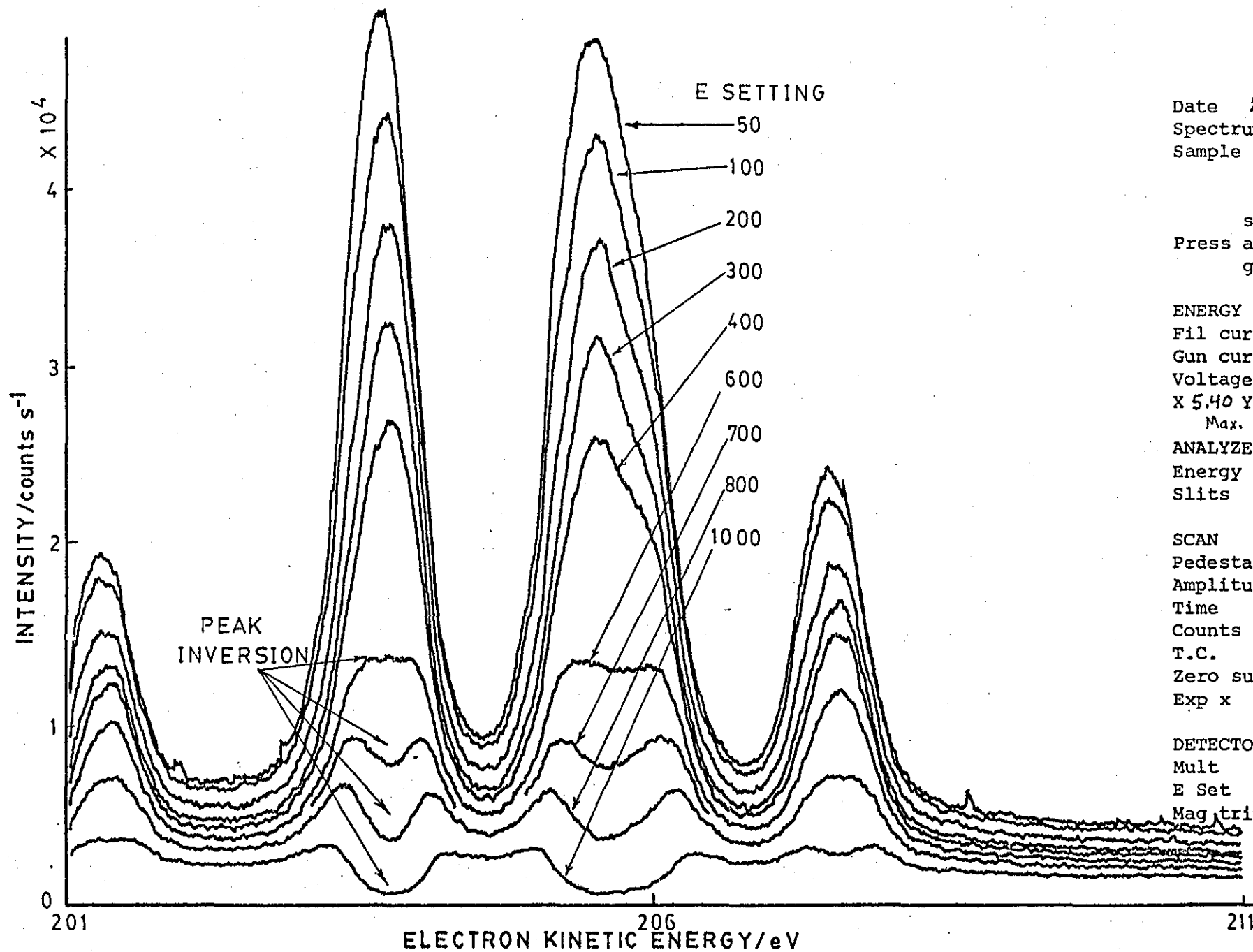
Date 24/7/78
Spectrum No. 1
Sample

Argon

sam 17 t
Press ana 2×10^{-6} t
gun 6×10^{-8} t

ENERGY SOURCE
Fil curr 3.1 A
Gun curr 100 µA
Voltage 5 kV
X 5.40 Y 3.32 F 10
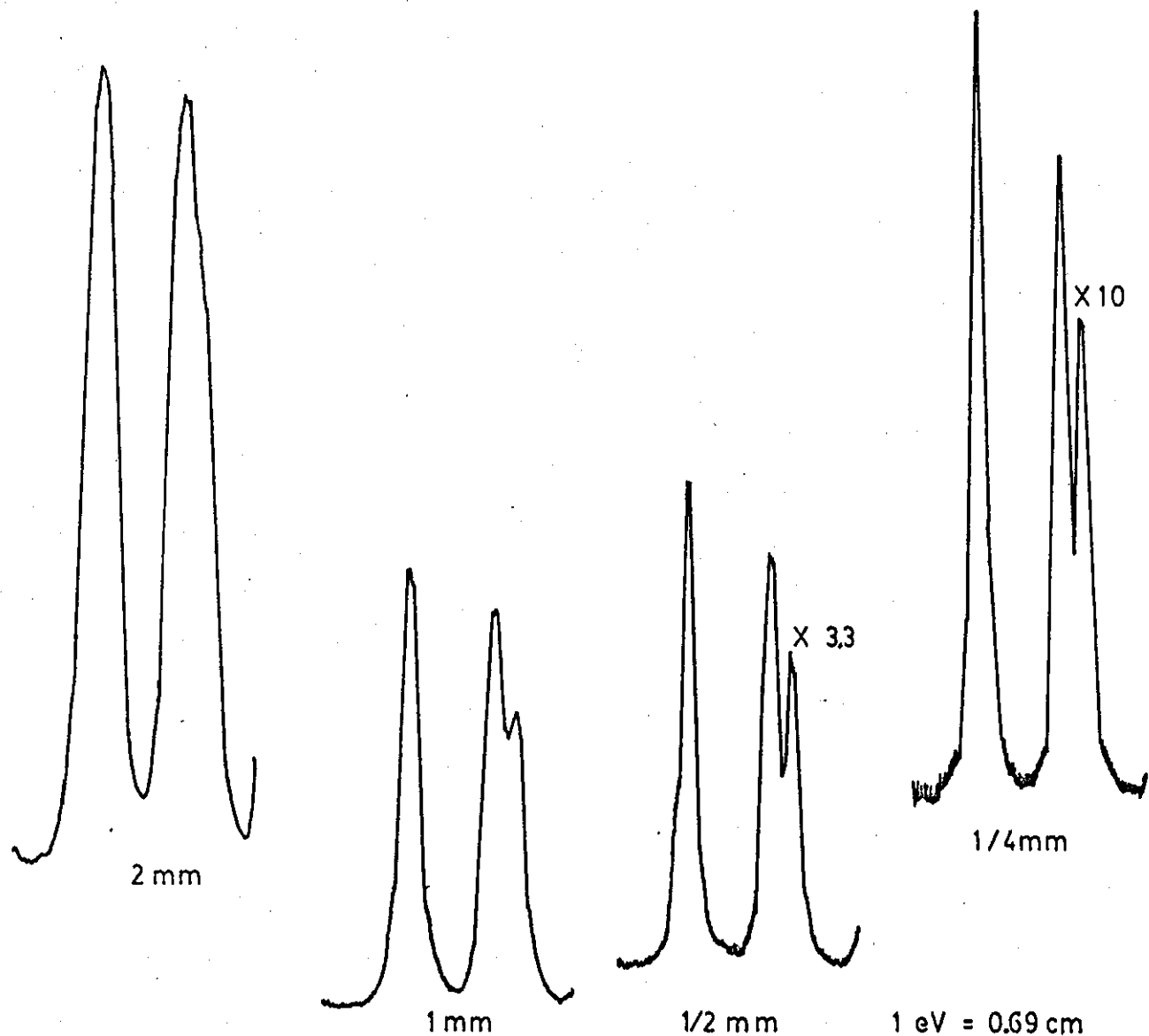Max. Fil curr. 480µA

ANALYZER
Energy 50 V
Slits 2 mm

SCAN
Pedestal 201 V
Amplitude 10 V
Time 100 s
Counts 3×10^4 s⁻¹
T.C. 0.33 s
Zero supp OFF
Exp x —

DETECTOR
Mult 3.2 kV
E Set Variable
Mag trim off mA

56

PEAK INVERSION
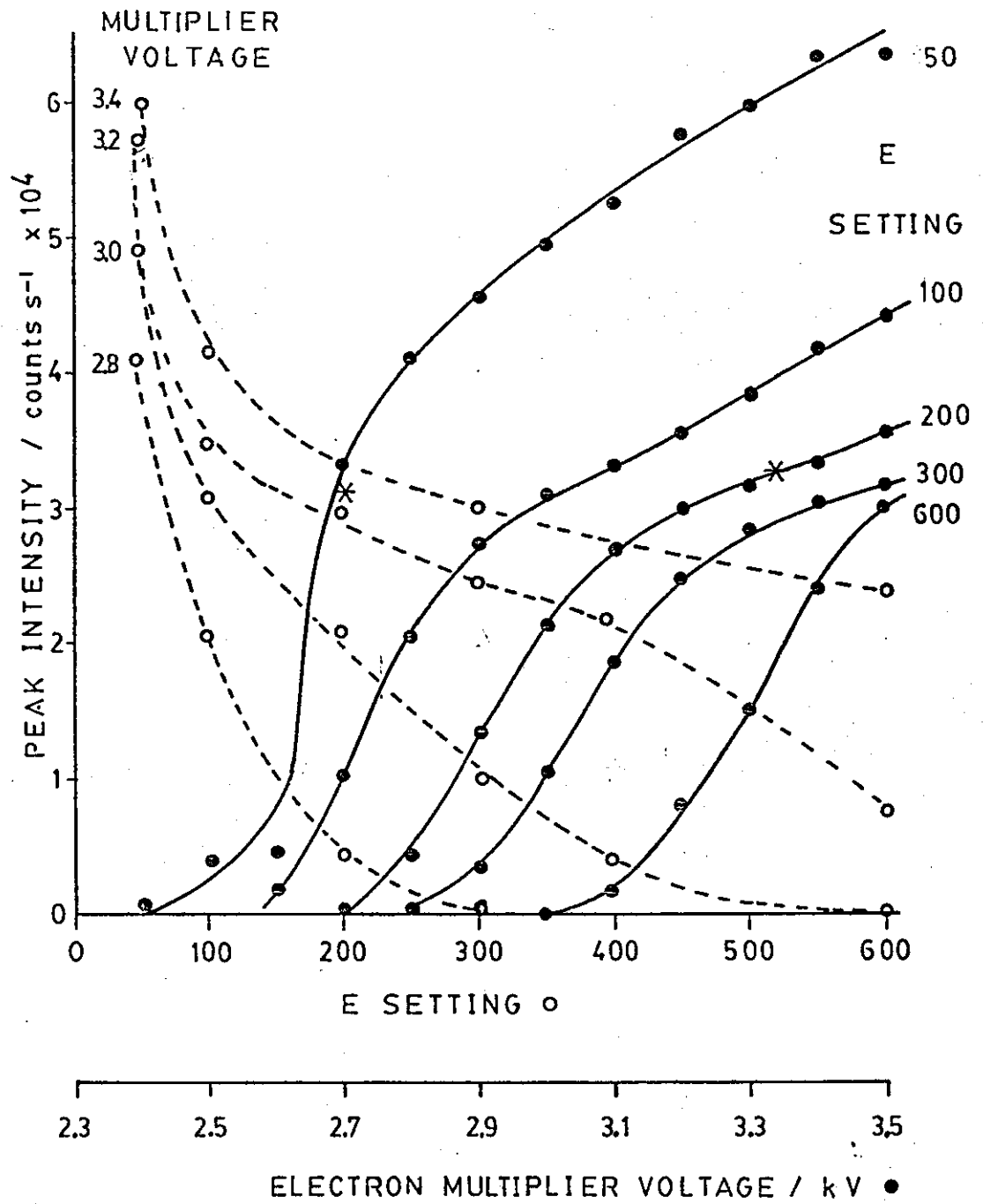
Fig. 3.9. Peak intensity as a function of E setting
and electron multiplier voltage.

increasing E setting.

In an explanation of this phenomena it must be remembered that the intensity of the Auger electrons and hence the output of the electron multiplier is independent of the E setting. The E setting only acts upon the electron multiplier signal to remove lower energy pulses. Referring to Fig. 3.6, if E is set at B then all of the Auger pulses will be counted. However if the pulse maximum is shifted below this fixed E setting then Auger pulses will be rejected and the indicated Auger signal will be reduced. This pulse maximum shift can occur at high Auger current intensity. Referring again to Fig. 3.8 it can be seen that the Auger intensity undergoes a great increase in intensity when a strong peak in the spectrum is scanned. Thus if E is set close to, but less than, a pulse distribution maximum then as a peak is scanned the increasing Auger signal reduces the electron multiplier gain, the pulse distribution maximum shifts to below the E setting, and this results in a decrease of the recorded Auger signal i.e. peak inversion.

This study has not revealed the definite electron multiplier pulse distribution. It does however indicate that the distribution is wide as a spectrum can still be recorded when E is set at 1000. Also the pulse height maximum appears to be less that 600 (E) as this is the setting at which peak inversion becomes quite noticable (Fig. 3.8). A pulse height selector would probably be a useful addition to the instrument.

3.4.3. Electron Multiplier Voltage

Increasing the voltage of the electron multiplier will increase its gain and the intensity of the output signal.

Fig. 3.9 shows the variation of intensity with multiplier voltage at different E settings. It also shows the variation of intensity with E setting, at different multiplier voltages. The intensity at an E setting of 100 and a multiplier voltage of 3.2 kV is ca. 35,000 counts s^{-1}.

The curves show plateaux on the intensity vs. multiplier voltage curves for E settings up to 300. An E setting of 100 was chosen for most work because it gave high intensity. An E setting of 50 gave higher intensity but it produced a noisy signal.

Plateaux on the intensity vs. E setting curves were obtained for multiplier voltages of 3.2 and 3.4 kV. A multiplier voltage of 3.2 kV was chosen for most work to give the multiplier a longer life; this voltage lies on the plateau of intensity vs. multiplier voltage
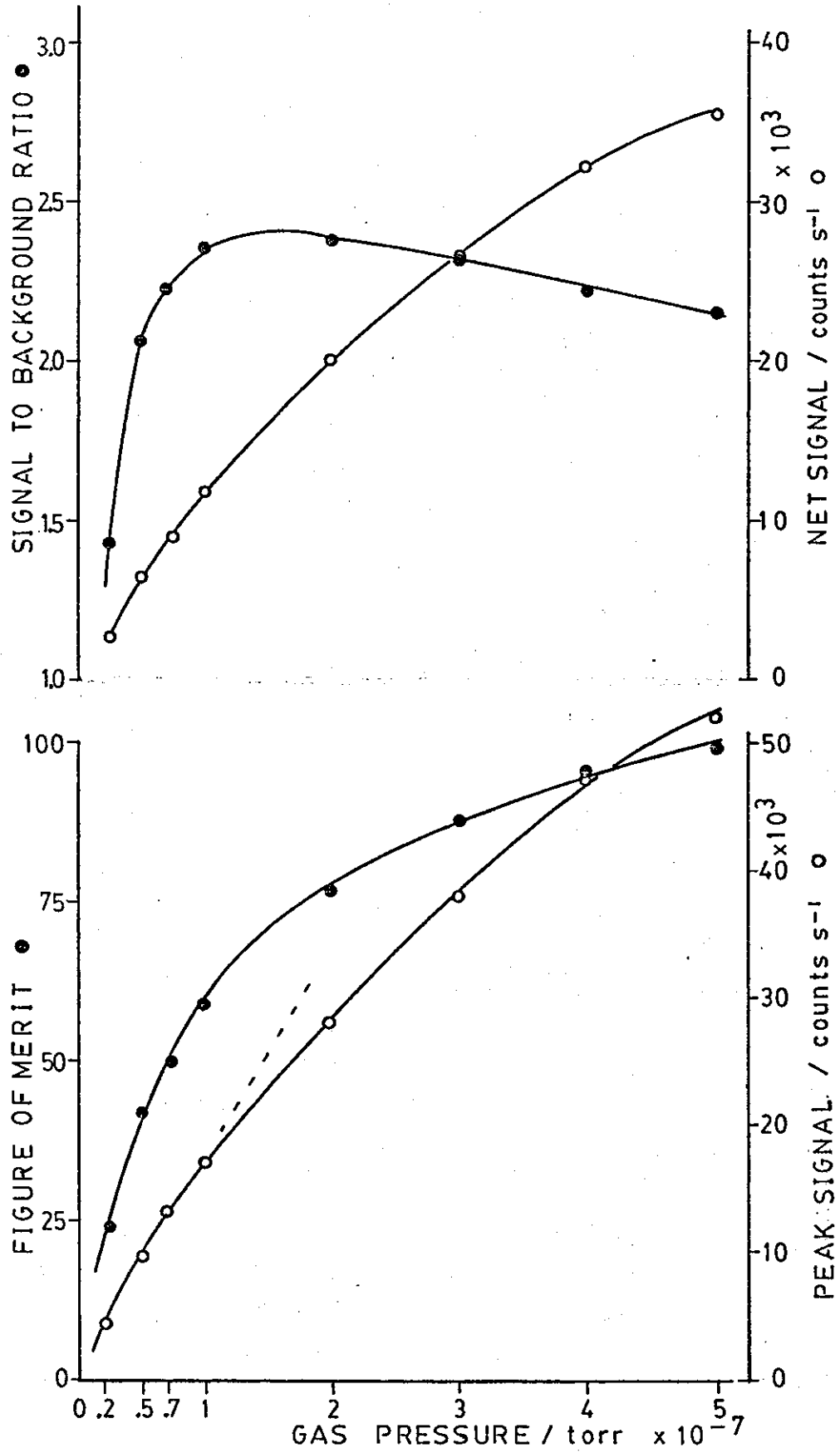
Fig. 3.10. The effects of sample gas pressure, as measured in the electron gun stack. (Nitrogen, excited by primary electrons of 5 kV and 20 μA.)

for the 100 E setting curve.

For this particular count rate (30 – 50,000 counts s^{-1}) an E setting of 200 and a multiplier voltage of 3.3 kV would probably be a better choice as both settings would lie on the plateau of a curve (see Fig. 3.9, the points are marked by an asterix). However the calculated signal–to–background ratios and figures of merit for both these sets of conditions were similar. Curves for lower count rates also indicated the choice of 200 E and 3.3 (or higher) kV.

A more detailed examination of the pulse distribution and how it varies with E setting, multiplier voltage, and count rate could possibly result in the selection of conditions which would give lower signal backgrounds.

3.5. The Sample Introduction System

The only parameter in the system is the amount (pressure) of gas in the spectrometer collision chamber. Unfortunately this is not measured in the system used. The amount of gas in the spectrometer is monitored by either the gas pressure in the analyzer or in the electron gun stack. Both of these are indicated on the appropriate ion vacuum gauge (Fig. 2.5). The two pressures are related to one another by a straight line relationship.

The pressure in the gas expansion chamber does not appear to affect the peak intensity for a given sample gas pressure (as indicated by either the gun or analyzer pressure gauge). A pressure between 10 and 20 torr was usually used.

The peak intensity, net intensity, signal–to–background ratio, and figure of merit varies with the sample (gun/analyzer) gas pressure. The effect of gas pressure is shown in Fig. 3.10. Thompson et al. [4] interpreted the decrease in signal–to–background ratio after a pressure of 2 – 3 x 10^{-7} torr as due to the increased scattering of the Auger electrons. The dead time of the counting system at these high count rates may also be contributing to the decrease in the signal–to–background ratio (sec. 5.6.4) as it would have a larger effect on I_p than I_b.

A gas pressure of 4 x 10^{-7} torr was used in the determination of limits of detection. This pressure gave a detection limit of approximately two thirds of that obtained at a pressure of 2 x 10^{-7} torr (Table 5.5).

3.6. Time Constant and Sweep Time

The selection of a time constant and sweep time for recording a spectrum has been discussed by Sevier [5] and by Barrie [6]. A good selection of time constant and sweep time will result in a "truer" spectrum. Time constant effects are a reduction of the height of the maximum, a shift of the centre, and an increase in FWHM. However areas under distorted curves are still correct. In general the shorter the time constant or the slower the sweep time, the more faithful the reproduction of the resolution curve. Two suggested expressions relating these constants are: [5,6]

$$\text{Time Constant} \leq \frac{(0.2)\ (\text{FWHM})}{\text{Sweep Rate}} \quad \frac{\text{eV}}{\text{eV s}^{-1}}$$

and

$$\text{Sweep Rate} \leq \frac{(.05)\ (\ E^{\frac{1}{2}})}{\text{Time Constant}} \quad \frac{\text{eV}}{\text{s}}$$

These two expressions are equivalent except for the choice of constant i.e. 0.2 or 0.05. From these two expressions

and

$$de = e\ \frac{dr}{2r} \quad (\text{sec. } 3.3.2)$$

the following expression has been developed:

$$\text{Time Constant} \leq \frac{(\text{Analyzer Energy})\ (\text{Slit Width})\ (\text{Sweep Time})}{(\text{Sweep Amplitude})\ (1000\ \text{or}\ 4000)}$$

where the units are:

Analyzer Energy and Sweep Amplitude — volts

Slit Width — millimeters

Sweep Time — seconds

Time Constant — seconds

The constant term in the denominator is either 1000 or 4000 depending on the faithfulness of reproduction required. The lower value will probably give a time constant adequate for most work.

Fig. 4.1. The general features of an Auger spectrum.

C AUGER OF C₂H₂
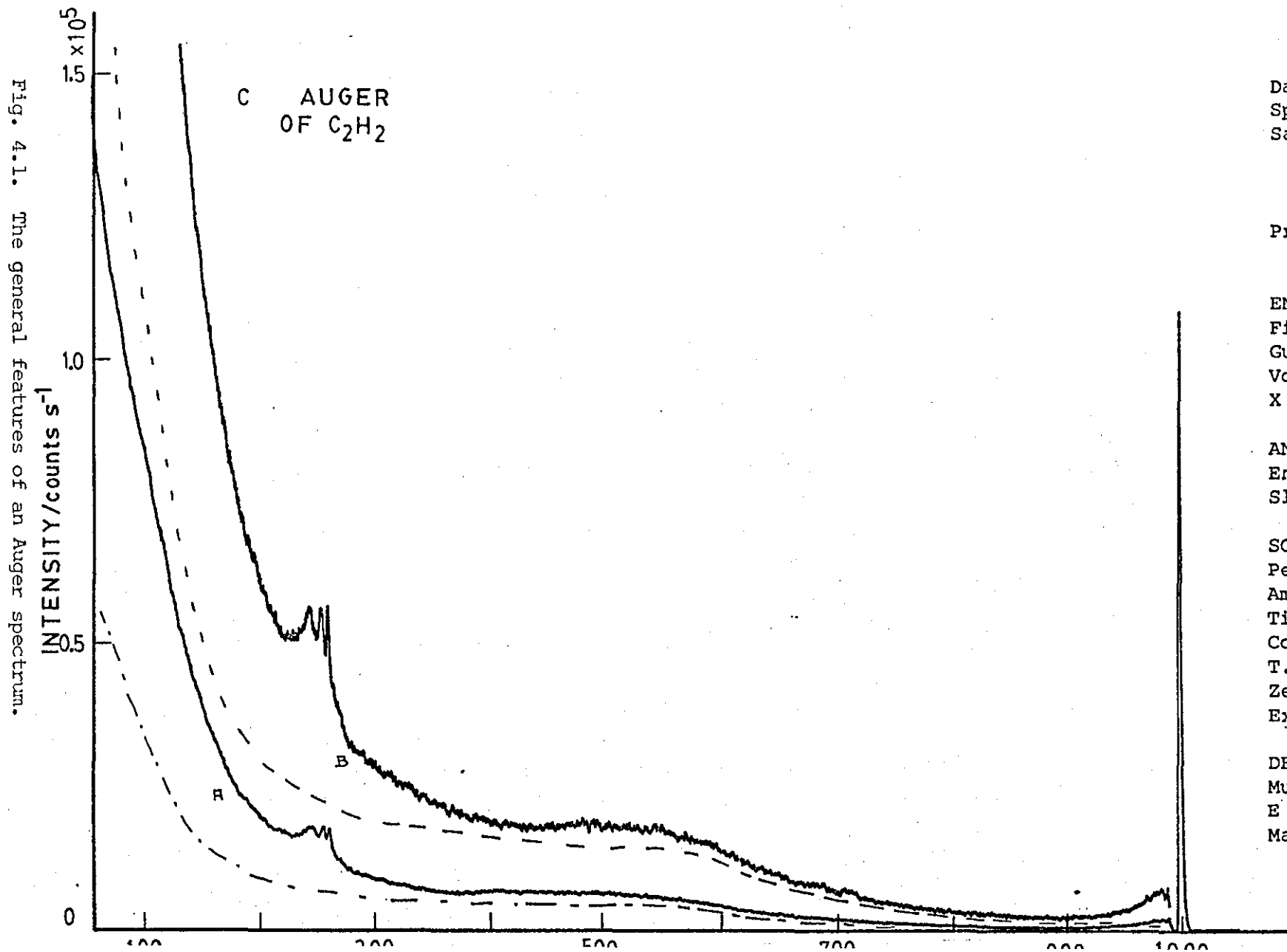
Date &1/3/78
Spectrum No. 1
Sample
    C₂H₂ ——————
    no gas — — — —
    sam   7.5   t
Press ana 8×10⁻⁶ t
    gun   1×10⁻⁷   t

ENERGY SOURCE
Fil curr   2.6   A
Gun curr   50   µA
Voltage   1   kV
X 4.67 Y 5.34 F 7.52
    Max gun curr   530µA
ANALYZER
Energy   50   V
Slits   2   mm

SCAN
Pedestal   50   V
Amplitude 1000   V
Time   300   s
Counts 1×10⁵/3×10⁴ s⁻¹
T.C.   0.33   s
Zero supp   —
Exp x   —

DETECTOR
Mult   3.2   kV
E Set   100
Mag trim   mA

Chapter 4

QUALITATIVE ANALYSIS

4.1.   Introduction

The analytical potential of gas-phase Auger electron spectroscopy has been discussed by Thompson [1,2] and Carlson. [3] The previous work done in this field at Loughborough University of Technology is described by Wooliscroft [4] and Hewitt. [5]

This study has been concerned with investigating the possibility of elemental and molecular analysis of pure and simple mixtures of gases. Previous studies at Loughborough dealt mostly with pure gases and the interpretation of their spectra. The experimental results are preceeded by a discussion of the Auger process, and Auger spectra and their interpretation.

4.2.   The Auger Spectrum

The Auger spectrum of a gas molecule is superimposed on a background spectrum of scattered electrons. The general features of an Auger spectrum are illustrated in Fig. 4.1. This spectrum is very similar to that given by Bouwman [6] for a solid bombarded by electrons. The general features of the spectrum are explained by Bouwman [6] as well as by Wooliscroft [4] and Hewitt. [5]

The Auger spectra of gases are complex and not easily interpreted. An empirical method of spectra interpretation has been suggested by Thompson et al. [2,7] and used to assign possible Auger transitions of several gases (sec. 4.4).

4.3.   The Auger Process

The Auger process has been explained many times in the literature and in texts [8,9,10,11] as well as in the previous theses [4,5] on this subject at Loughborough. This explanation will therefore be brief. It will, however, relate the Auger process to related analytical phenomena and their analytical spectroscopic techniques.

The Auger process is one of the phenomena occurring upon bombarding a material with energetic electrons, photons, or other forms of energy (e.g. energetic ions). This work is concerned with excitation by energetic electrons, therefore unless stated otherwise, it is this mode of the technique referred to. Bombardment of a gas (in a metal collision chamber) with energetic electrons causes the emission of a collection of backscattered secondary electrons (Fig. 4.1).
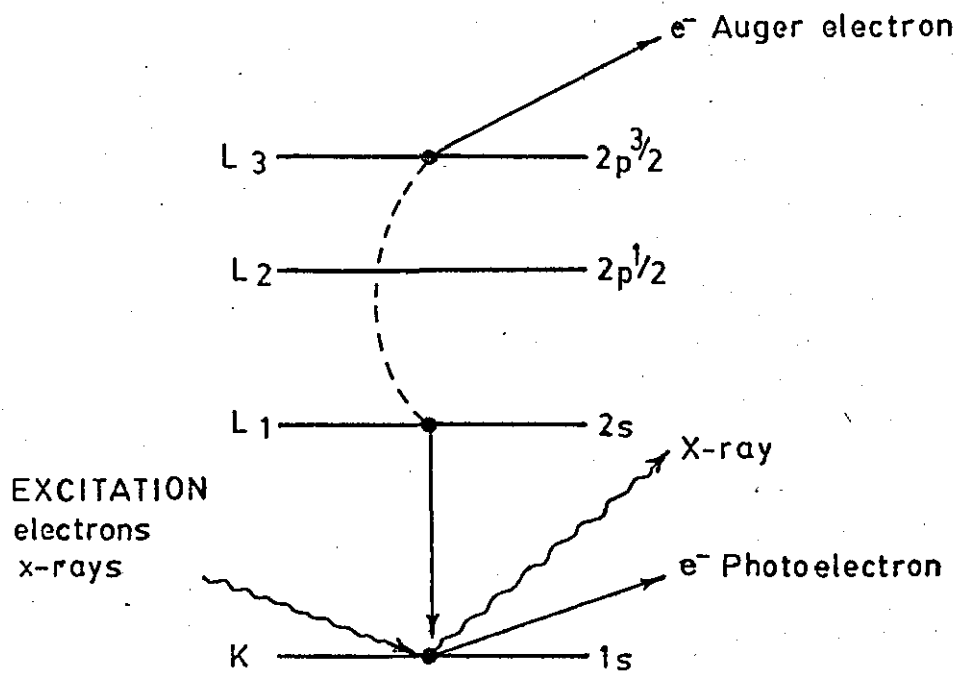
Fig. 4.2. The Auger and related processes of analytical importance.

KLL AUGER TRANSITIONS
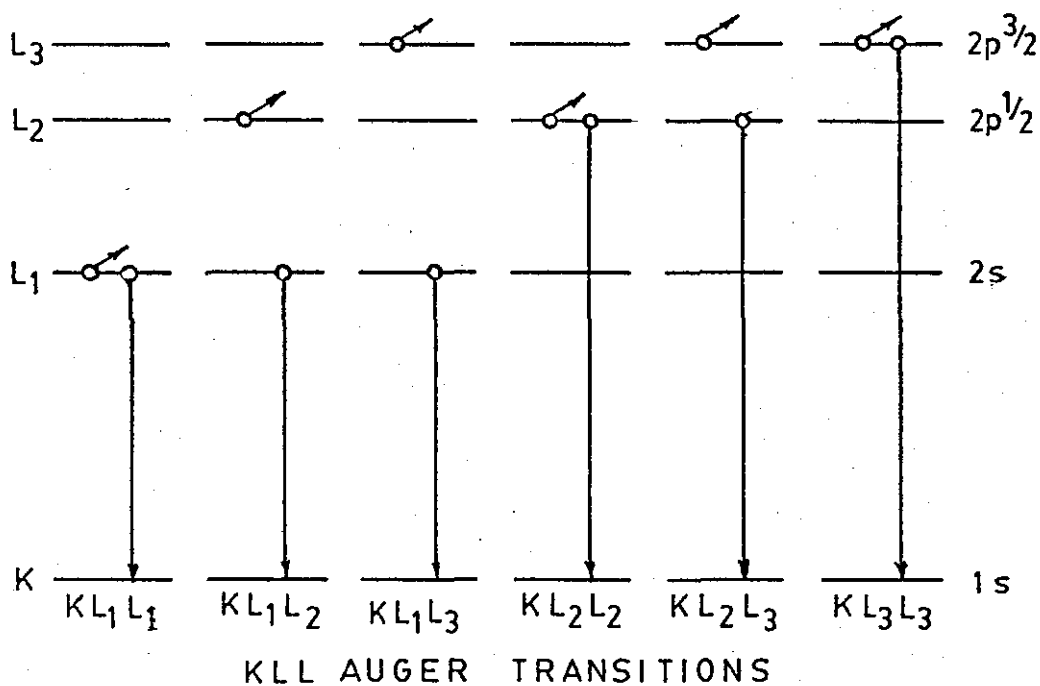
Fig. 4.3. KLL Auger transitions assuming j-j coupling.

The Auger peaks superimposed on this background are the result of a non-radiative de-excitation of core-ionized atoms.

Assume that an electron from inner shell X has been removed from the atom by ionization with energetic electrons or x-rays (Fig. 4.2). The ion thus produced may de-excite by the emission of a characteristic photon (x-ray) or by a radiationless transition. In the latter case two less tightly bound electrons are shifted out of their orbitals by Coulombic repulsion. One electron, from the Y level, fills the vacancy of level X. The other electron, from the Z level, is ejected. The ejected electron, the Auger electron, is designated an XYZ electron. Fig. 4.3 shows the KLL Auger transitions when j-j coupling in an atom is assumed. For light elements the coupling is nearly pure L-S with five lines, for high atomic number elements it is nearly pure j-j with six lines. Intermediate atomic number elements have intermediate coupling and as many as nine lines. [12]

The analytical techniques of x-ray fluorescence spectrometry, electron probe microanalysis, and x-ray photoelectron spectroscopy are related to Auger electron spectrometry. This relationship is through the processes necessary for, or alternate to, the Auger process and through their sometimes similar or complimentary applications.

Fig. 4.2 shows the ejection of a photoelectron due to the initial ionization of an atom. If the ionization is caused by x-ray excitation then the associated technique is x-ray photoelectron spectroscopy. The de-excitation of the ions formed always takes place by both the Auger process and photon emission. The Auger process dominates for low atomic number elements but the fluorescent yield of photons increases with atomic number. X-ray fluorescence spectrometry and electron probe microanalysis are therefore important for fluorine and higher atomic number elements, although spectrometers for gaseous studies of soft x-rays are known. [13]

Carlson[14] has discussed the similar application of these techniques. They each yield information on binding energies of inner shells and hence are capable of elemental analysis.

4.4. Spectral Interpretation

In the previous work done at Loughborough spectral interpretation has been done by empirical methods. [2,7] One of these methods will be outlined here.

The XYZ Auger electron energies are estimated using the equation

$$E_{XYZ} = E_X - E_Y - E_Z \qquad 4.1$$

where the Auger process is effectively considered to be an internal x-ray photoeffect. E_{XYZ} is the calculated Auger energy, E_X is the energy of the initial vacancy level, and E_Y and E_Z are the energies of the levels from where the "down" and Auger electrons originate, respectively. The appropriate ionization energies must be obtained from the literature. This equation does not however take into account the shifts in bonding energy, usually termed relaxation, that occur as a result of ionization. The equation is therefore modified to

$$E_{XYZ} = E_X - E_Y - E_Z - E_R \qquad 4.2$$

where E_R is the relaxation energy.

The relaxation energy is estimated from the difference between E_{XYZ}, calculated using equation 4.1, and the experimental Auger energy for the highest energy peak in the Auger spectrum. The assumption is made that all the transitions possible in a given case have constant relaxation energy. This is a crude assumption, however the relaxation energy calculated by this method for S in H_2S is acceptable [15] for the high energy Auger states, but is low for the lower energy states.

The procedure followed is to determine the ground state configuration of the molecule and the appropriate ionization energies (binding energies) of the various energy levels. The possible Auger transitions are then determined (Fig. 4.3). The calculation of the relaxation energy depends on correctly identifying the peak which corresponds to the highest energy normal Auger transition. An Auger spectrum may have satellite and autoionization lines which have an energy greater than those due to this transition. [16,17] Independant experiments can be used to help in identifying these. The appearance potential of the doubly ionized molecular ion, obtained from mass spectrometry, can also be used for choosing the highest energy normal peak. The relaxation energy is then calculated using equation 4.2 as outlined previously. The Auger energies of the possible transitions are

then calculated using this value of E_R and equation 4.2.

These empirical methods have been used for assigning Auger transitions in the spectra of C_2H_2, H_2S, SO_2, and NH_3; [4] also in CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. [5]

Examples of this method for carbon monoxide, carbon tetrafluoride, and nitrogen gas are given. The necessary data is that of Siegbahn. [16] Tables 4.1, 4.2, 4.3, and 4.4 give molecular energy levels, their corresponding binding energies, the possible Auger transitions, the calculated Auger energies, and the experimental Auger energies.

As the possible final states are the same for both the C and O Auger transitions of CO it is obvious that the energy spacings within the C and the O spectra will be similar, but shifted against each other by 246.2 eV which is the energy difference between the two initial energy states. However the intensities will be different because electrons in orbitals centered on the same atom as the initial vacancy participate in the transition.

The experimental peaks corresponding to the high energy transitions for CO (Table 4.1) have been chosen because of their agreement with the appearance potentials of the doubly ionized molecule (295.9 or 542.1 – 41.8 = 254.1 or 500.3 eV). However Karlsson [18] has used an energy of 500.8 eV for the Auger transition to the $1\pi\,3\sigma$ state, the peak due to the transition to the $3\sigma\,3\sigma$ was calculated to be absent. Karlsson approximated the transition energies using equation 4.3.

$$E_{kin} = E_{max} - (\Delta E(X) + \Delta E(Y))$$ 4.3

where

E_{kin} = the Auger electron energy.

E_{max} = the Auger electron energy of the transition to two vacancies in the outermost orbital.

$\Delta E(X)$, $\Delta E(Y)$ are the differences in binding energy from the outermost orbital for those electrons participating in the Auger transition.

The energies calculated by Karlsson, using equation 4.3, for the oxygen spectrum of CO are identical to those obtained using equation 4.2 when 500.8 eV is also used as the Auger transition to the $1\pi\,3\sigma$ state (Table 4.2). The two equations are equivalent.

The calculated Auger energies of carbon and fluorine in carbon tetrafluoride (Table 4.3) show surprisingly good agreement

TABLE 4.1

CALCULATED AND EXPERIMENTAL AUGER ENERGIES OF
CARBON AND OXYGEN IN CARBON MONOXIDE

Orbital	C1s	O1s	1σ	2σ	1π	3σ
Binding Energy (eV)	295.9	542.1	38.3	20.1	17.2	14.5

KLL[1] Auger Transitions	Carbon Energies		Oxygen Energies	
	Calculated E_R = 12.9 eV	Experimental	Calculated E_R = 12.5 eV	Experimental
$3\sigma 3\sigma$	254.0	254.0 (2)	500.6	500.6 (4)
		253.8 252.9		
		.6 .8		
		.4 .6		
		.2 .5		
		.1 .1		
$1\pi 3\sigma$	251.3	251.9 (2)*	497.9	496.4 (4)
		250.5 (2)*		
				495.0 (4)**
$1\pi 1\pi$	248.6	250.5 (2)	495.2	494.6 (4)*
				494.3 (4)*
$2\sigma 3\sigma$	248.4	250.2 (2)	495.0	494.0 (4)
$2\sigma 1\pi$	245.7	245.5 (2)**	492.3	491.9 (6)**
$2\sigma 2\sigma$	242.8	242.9 (2)**	489.4	488.0 (5)
		239.7 (3)		485.4 (5)
		235.1 (7)		
$1\sigma 3\sigma$	230.2	230.8 (7)**	476.8	
$1\sigma 1\pi$	227.5		474.1	
$1\sigma 2\sigma$	224.6	220.4 (7)	471.2	469.3 (9)**
				458.9 (9)
$1\sigma 1\sigma$	206.4		453.0	448.4 (9)

1. Preceeded by C1s or O1s

    Errors in parentheses.

    Binding energies and experimental data from reference 16.

*   Agreement between calculated and experimental energies (including error) within +/- 0.5 eV.

** Agreement between calculated and experimental energies, within the experimental error.

TABLE 4.2

CALCULATED AND EXPERIMENTAL AUGER ENERGIES OF

CARBON AND OXYGEN IN CARBON MONOXIDE

KLL[1] Auger Transitions	Carbon Energies		Oxygen Energies	
	Calculated[2] $E_R = 10.2$ eV	Experimental	Calculated[3] $E_R = 9.6$ eV	Experimental
$3\sigma\,3\sigma$	256.7	256.1 (2)*	503.5	
$1\pi\,3\sigma$	254.0	254.0 (2) 253.8 252.9 .6 .8 .4 .6 .2 .5 .1 .1	500.8	500.6 (4)
$1\pi\,1\pi$	251.3	251.9 (2)* 250.8 (2)	498.1	496.4 (4)
$2\sigma\,3\sigma$	251.1	250.5 (2)* 250.2 (2)	497.9	
$2\sigma\,1\pi$	248.4		495.2	495.0 (4)** 494.6 (4) 494.3 (4) 494.0 (4)
$2\sigma\,2\sigma$	245.5	245.5 (2)** 242.9 (2)	492.3	491.9 (6)** 488.0 (5)
$1\sigma\,3\sigma$	232.9	239.7 (3) 235.1 (7)	479.7	485.4 (5)
$1\sigma\,1\pi$	230.2	230.8 (7)**	477.0	
$1\sigma\,2\sigma$	227.3	220.4 (7)	474.1	469.3 (9)
$1\sigma\,1\sigma$	209.1		455.9	458.9 (9) 448.4 (9)

1. Preceeded by Cls or Ols.

2. Selection of 254.0 eV for Cls $1\pi\,3\sigma$ transition on basis of O E_R of 9.6 eV.

3. Selection of 500.8 eV for Ols $1\pi\,3\sigma$ transition indicated by Karlsson[18].

Errors in parentheses.

Binding energies and experimental data from reference 16.

*, ** refer to Table 4.1.

TABLE 4.3

CALCULATED AND EXPERIMENTAL AUGER ENERGIES OF

CARBON & FLUORINE IN CARBON TETRAFLUORIDE

Orbital	C1s	F1s	$1a_1$	$1t_2$	$2a_1$	$2t_2$	$1e$	$1t_1$	$3t_2$
Binding Energy (eV)	301.8	695.2	43.8	40.3	25.1	22.2	18.5	17.4	16.1

KLL^1 Auger Transitions	Carbon Energies		Oxygen Energies	
	Calculated $E_R = 10.6$ eV	Experimental	Calculated $E_R = 10.9$ eV	Experimental
$3t_2\ 3t_2$	259.0	259.0 (4)	652.1	652.1 (5)
$1t_1\ 3t_2$	257.7	257.6 (4)**	650.8	651.7 (5)*
$1t_1\ 1t_1$	256.4	256.1 (4)**	649.5	650.0 (5)**
$1e\ 3t_2$	256.6		649.7	
$1e\ 1t_1$	255.3		648.4	648.7 (5)**
$1e\ 1e$	254.2	254.5 (3)**	647.3	
$2t_2\ 3t_2$	252.9	252.8 (4)**	646.0	646.3 (5)**
$2t_2\ 1t_1$	251.6	251.4 (3)**	644.7	644.7 (5)**
$2t_2\ 1e_1$	250.5	250.3 (4)**	643.6	
$2t_2\ 2t_2$	246.8	246.8 (4)**	639.9	639.7 (6)**
$2a_1\ 3t_2$	250.0		643.1	642.9 (5)**
$2a_1\ t_1$	248.7	248.6 (4)**	641.8	641.4 (5)**
$2a_1\ 1e$	247.6		640.7	
$2a_1\ 2t_2$	243.9		637.0	
$2a_1\ 2a_1$	241.0	241.5 (5)**	634.1	635.6 (6)
				631.0 (7)
$1t_2\ 3t_2$	234.8		627.9	
$1t_2\ 1t_1$	233.5		526.6	
$1t_2\ 1e$	232.4		625.5	
$1t_2\ 2t_2$	228.7	227.5 (4)	621.8	
$1t_2\ 2a_1$	225.8		618.9	
$1t_2\ 1t_2$	210.6		603.7	
$1a_1\ 3t_2$	231.3	231.5 (4)**	624.4	624.2 (6)**
$1a_1\ 1t_1$	230.0		623.1	
$1a_1\ 1e$	228.9		622.0	
$1a_1\ 2t_2$	225.2		618.3	
$1a_1\ 2a_1$	222.3		615.4	616.6 (6)
$1a_1\ 1t_2$	207.1		600.2	
$1a_1\ 1a_1$	203.6		596.7	

1. Preceeded by C1s or F1s. Refer to Table 4.1 for comments.

TABLE 4.4

CALCULATED AND EXPERIMENTAL AUGER ENERGIES OF

NITROGEN IN NITROGEN GAS

Orbital	$N1s$	$\sigma_g 2s$	$\sigma_u 2s^+$	$\sigma_u 2s$	$\pi_u 2p$	$\sigma_g 2p$
Binding Energy (eV)	409.9	37.3	25.0	18.6	16.8	15.5

KLL[1] Auger Transitions	Nitrogen Energies[2] Calculated $E_R = 11.7$ eV	Experimental	Nitrogen Energies[3] Calculated $E_R = 12.2$ eV	Experimental
$\sigma_g 2p$ $\sigma_g 2p$	367.2	367.2 366.9	366.7	366.7 (2)
$\pi_u 2p$ $\sigma_g 2p$	365.9	365.4 (3)*	365.4	365.2 (4)**
$\pi_u 2p$ $\pi_u 2p$	364.6			
$\sigma_u 2s$ $\sigma_g 2p$	364.1	364.1 (4)**	363.6	363.7 (5)**
$\sigma_u 2s$ $\pi_u 2p$	362.8	362.8 (4)**	362.3	362.7 (5)**
$\sigma_u 2s$ $\sigma_u 2s$	361.0	360.4 (3)* 359.1 (3)	360.5	360.4 (2)** 358.9 (2)
$\sigma_u 2s^+$ $\sigma_g 2p$	357.7	357.2 (4)*	357.2	357.1 (3)**
$\sigma_u 2s^+$ $\pi_u 2p$	356.4	352.1 (5)	355.9	354.9 (6)*
$\sigma_u 2s^+$ $\sigma_u 2s$	354.6	352.1 (5)	354.1	352.7 (6) 350.6 (6)
$\sigma_u 2s^+$ $\sigma_u 2s$	348.2		347.7	348.0 (6)**
$\sigma_g 2s$ $\sigma_g 2p$	345.4		344.9	
$\sigma_g 2s$ $\pi_u 2p$	344.1		343.6	342.6 (4)
$\sigma_g 2s$ $\sigma_u 2s$	342.3	342.2 (5)** 339.2 (5)	341.8	339.3 (5)
$\sigma_g 2s$ $\sigma_u 2s^+$	335.9		335.4	337.6 (6)
$\sigma_g 2s$ $\sigma_g 2s$	323.6			332.9 (7) 315.2 (9)

+ This line is interpreted as due to a shake-up at the ionization of a $\sigma_u 2s$ electron.

1. Preceeded by N1s.

2. Experimental data from reference 16.

3. Experimental data from reference 17, 0.2 eV added to each reading to adjust for differences in reference energy of argon.

Refer to Table 4.1 for additional comments.

with the experimental data of Siegbahn.[16] Table 4.4 uses experimental data from both Siegbahn[16] and Moddeman.[17] The agreement between calculated and experimental transition energies is better for Moddeman's data.

4.5. Auger Spectra of Atmospheric Gases

The Auger spectra of N_2, O_2, Ar, Ne, CO, CO_2, NO, NO_2, H_2S, and SO_2 as well as C_2H_2, CH_4, N_2O, and NH_3 have been obtained on the VG AFM2 spectrometer and are in Appendix C. These spectra have been recorded on the same spectrometer and under similar conditions to allow an easier comparison of them. The actual conditions of analysis are recorded on each spectrum. In general, an Auger spectrum of each element in a compound has been obtained (except hydrogen); the spectra are recorded in 100 and 30 eV ranges and at analyzer energies of 50 eV and a slit width of 2 mm. Some spectra of higher resolution are also included.

Energy calibration of the spectra was performed by comparison with the energy of the $L_3M_{2,3}M_{2,3}$ ($^1D_2$) line of argon. The energy of this line was taken as that obtained by Siegbahn et al.[16] who quote a value of 203.47 eV. Wooliscroft[4] has discussed energy calibration more extensively. Energy calibration in this work has differed in that the calibrating gas has been mixed with the gas analyzed. Wooliscroft obtained the spectrum of the analyte and of argon alternately on the same graph paper, however the chart recorder is not capable of exactly reproducing the initial starting position. The use of an internal calibrating gas is recommended by the spectrometer manufacturer and as well it appears to be the common method used.[17,18]

An additional difference is that argon was also used for any spectrum beginning at an energy of x · 100 eV (x = 3, 4, 5, ...8). This was possible by first beginning to record the argon spectrum starting at 200 eV, at ca. 206 eV the pedestal voltage was stepped, in 100 eV steps, to the appropriate value. The accuracy of the stepping was checked by setting the pedestal voltage to 200.0, stepping to the appropriate starting energy of the analyte spectrum and then reading the pedestal voltage. Any slight variation (usually less that a few tenths of an eV) could then be corrected for in the energy assignments. Secondary standards could be used in a similar manner for spectra beginning at other energies.

5 B	6 C	7 N	8 O	9 F	10 Ne	
eV	200-300	300-400	450-550	550-700	700-850	KLL
	C_2H_2 CO CO_2 CCl_4 CH_4	N_2, NH_3 N_2O NO NO_2 N_2O_3	O_2 N_2O,CO NO , CO_2 NO_2 SO_2 N_2O_3	C_6F_6	Ne	
	14 Si	15 P	16 S	17 Cl	18 Ar	
	e.V	e.V	100-150	150-200	150-225	LMM
			SO_2 H_2S	CCl_4	Ar	
				35 Br	36 Kr	

Fig. 4.4. Gases studied by AES

4.6. Elemental Analysis of Gases

The approximate kinetic energies of Auger electrons from atoms can be easily calculated (sec. 4.4). The energies depend firstly on the binding energy of the shell in which the initial ionization takes place; this energy is characteristic of the element. Unlike the production of the corresponding x-ray which involves only one other energy level of the atom, Auger electron production involves two other energy levels. The energies of Auger electrons are therefore lower and less well defined then those of the corresponding x-rays. A chart of principal Auger electron energies is contained in Appendix B.

The KLL spectra of light elements are well separated; LMM spectra of S, Cl, and Ar do overlap, althought their main features are separated. The spectra are contained within a range of ca. 100 eV with their main peaks within 30 eV. Fig. 4.5 is a composite diagram of individual spectra of these elements in gases. Elemental qualitative analysis of a gas mixture is illustrated in Fig. 4.6. The presence of each of the elements (S, Cl, Ar, C, N, and O) is easily seen. A change in the chemical environment of an element can result in a shift of the Auger electron energies. This chemical shift may allow the same element, in different forms, to be determined simultaneously (sec. 4.7).

The limits of detection for the various elements are listed in Tables 5.4 and 5.5. In general detection limits of ca. 1 mol % or lower may be obtainable.

4.7. Molecular Analysis of Gases

4.7.1. General

High resolution AES has already [17] been shown to useful for molecular as well as elemental analysis of gases. Although the average energy of a KLL Auger process depends principally on the K binding energy the details of the spectra depend on the nature of the molecular ion. Moddeman [17] has reported the differences in the oxygen spectra of O_2, CO, NO, H_2O, and CO_2; in the carbon spectra of CO and CO_2; and for nitrogen in NO and N_2. The Auger spectra of gases are therefore not only characteristic of the element but also the molecule.

The approach followed here is that of comparing unknown spectra with a library of known spectra (Appendix C). An initial elemental analysis of the gas using its Auger spectra reduces the number of

FIG. 4.5

AUGER ELECTRON ENERGIES
OF
LIGHT ELEMENTS IN GASES

ELECTRON KINETIC ENERGY / eV

Fig. 4.6. Elemental qualitative analysis of a gas mixture.

A E S
QUALITATIVE ANALYSIS
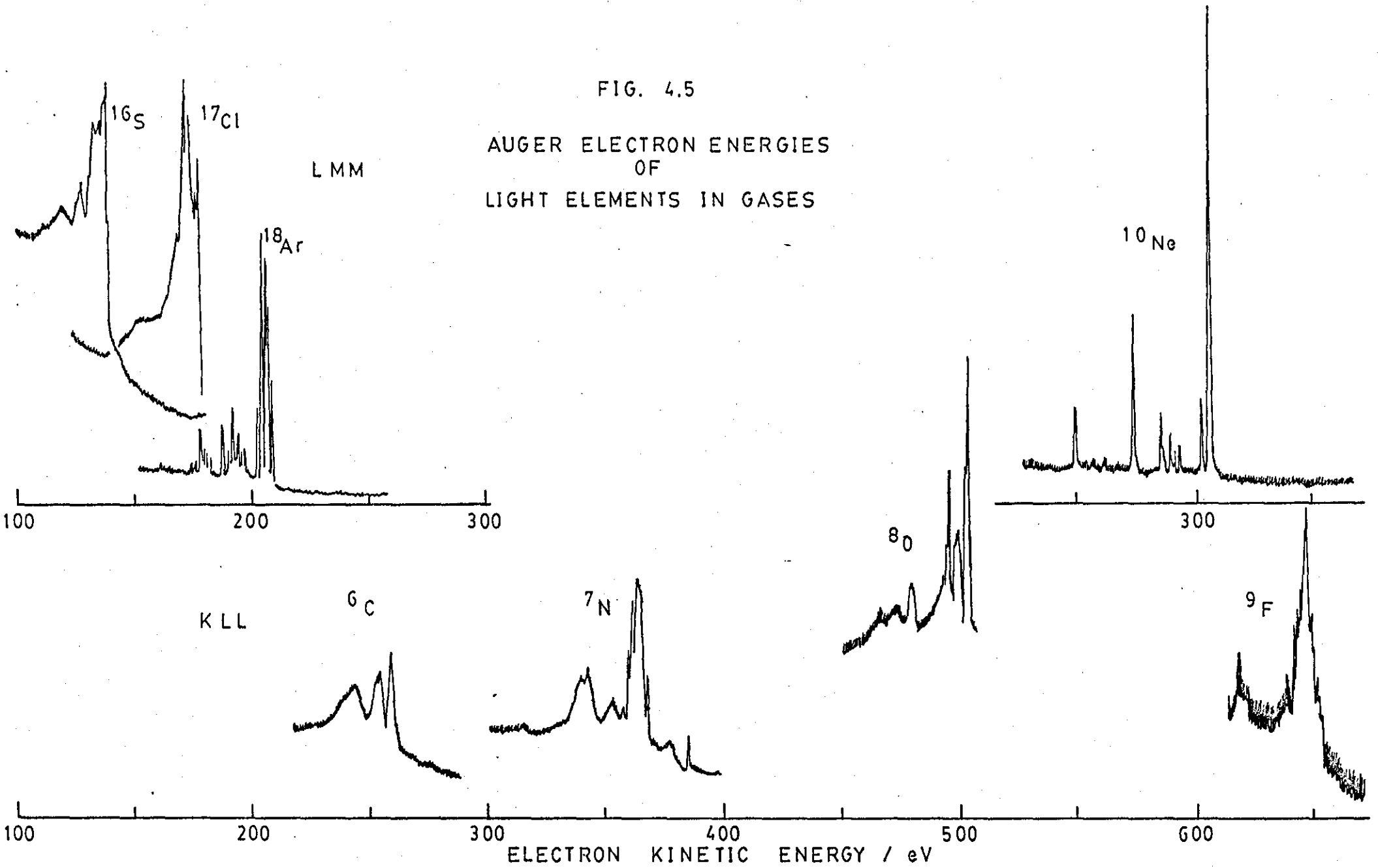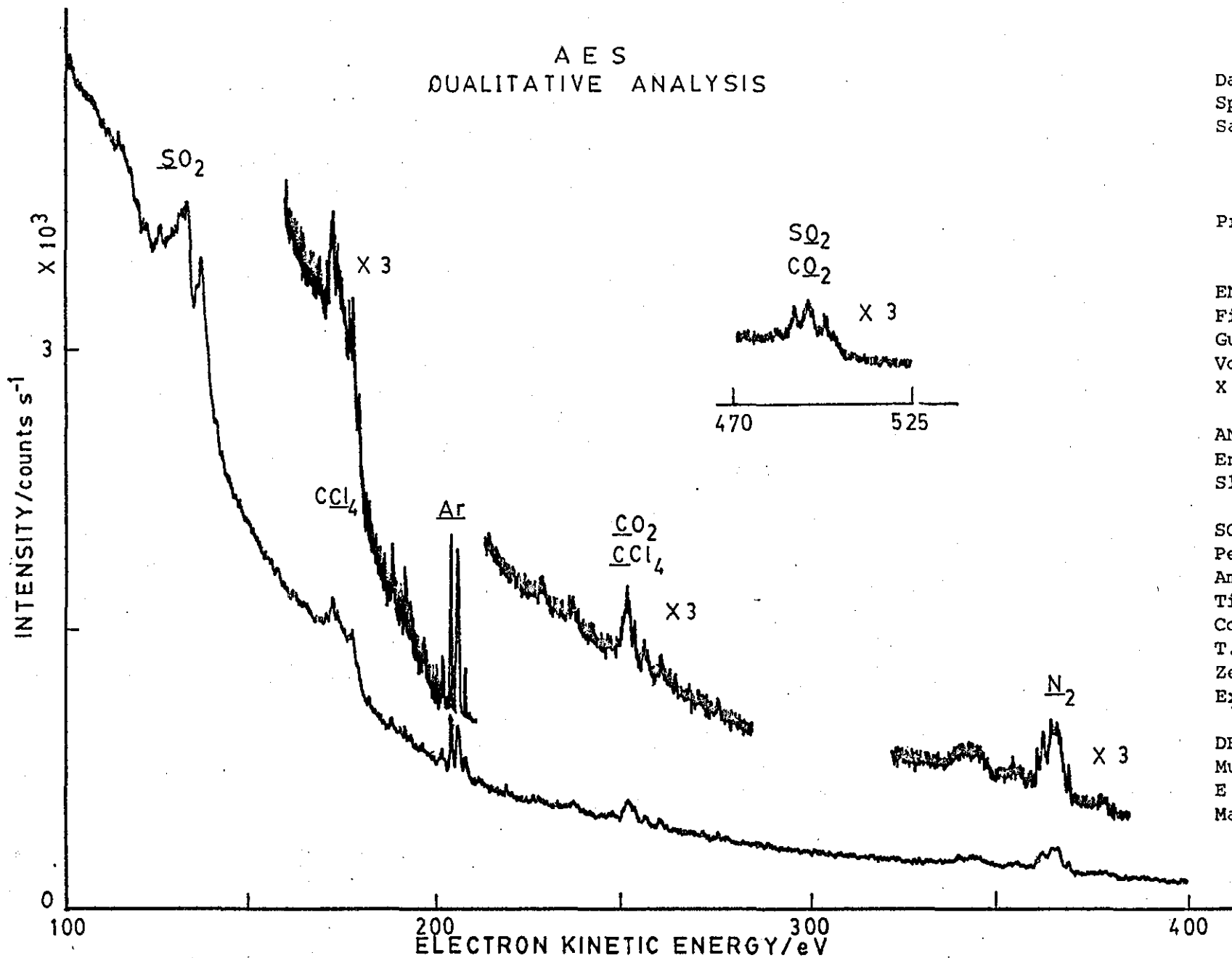
Date 11/5/78
Spectrum No.
Sample SO_2 20% Ar 20%
        CCl_4 20% N_2 20%
        CO_2 20%
        sam   10   t
Press ana   t
        gun 2×10^7 t

ENERGY SOURCE
Fil curr   3.4   A
Gun curr   200   μA
Voltage   5   kV
X   Y   F

ANALYZER
Energy   50   V
Slits   2   mm

SCAN
Pedestal   100   v
Amplitude   300   V
Time   300   s
Counts 3×10^3 s^{-1}
T.C.   0.33   s
Zero supp   —
Exp x   —

DETECTOR
Mult   3.2   kV
E Set   100
Mag trim   —   mA

76

spectra to be searched. The pure gases studied have proved to have very characteristic spectra. The problem area is the analysis of a gas mixture.

4.7.2   Analysis of CO and CO_2

The Auger spectra of CO and CO_2 contain the spectra of both C and O as expected (Fig. 4.7, 4.8). It is obvious that the two carbon spectra are different; the difference between the two oxygen spectra is less.

Fig. 4.9 shows a direct comparison of the carbon Auger spectra of CO, CO_2, and an equal molar mixture of both. The CO spectrum has more distinct peaks and is more intense (detection limit is ca. one third less, Table 5.4) than CO_2. The peaks at A and B in the mixture should allow the presence of CO in a mixture of the two to be detected more easily than CO_2 which would contribute the shoulder and the small peak at D.

A reverse situation exists for the O Auger spectra of the two. Fig. 4.10 shows the O spectra of CO, CO_2, a mixture of CO and CO_2 and O_2. The presence of the O_2 spectrum is to show the chemical shift. The CO_2, O spectra has more distinct peaks and is more intense (detection limit is ca. one half that of CO, Table 5.4). The peaks at A, B, C, and D indicate the presence of CO_2 in the mixture. The presence of CO, at high concentrations would be indicated by a decrease in the valley between peaks B and C; and a slight shifting of the peaks to higher energies.

The presence of both CO and CO_2 can be determined in a mixture of the two, provided the concentration ratio of one to the other is not extreme.

4.7.3.   Analysis of NO and NO_2

The Auger spectra of NO and NO_2 contain the spectra of both N and O.

Fig. 4.11 shows a direct comparison of the nitrogen Auger spectra of NO, NO_2, N_2O, and N_2. The spectrum of NO is slightly more distinct and is more intense (detection limit is ca. one third less, Table 5.4) than NO_2. The peaks at A, B, C, and D would indicate the presence of NO in a mixture of the two.

A comparison of their O spectra (Fig. 4.12) shows less distinction between the two compounds. The NO again has a lower detection limit but the two spectra have equally distinct peaks. The main differences are the peaks at A, B, and C.

Fig. 4.7. Carbon and oxygen Auger specta of CO.
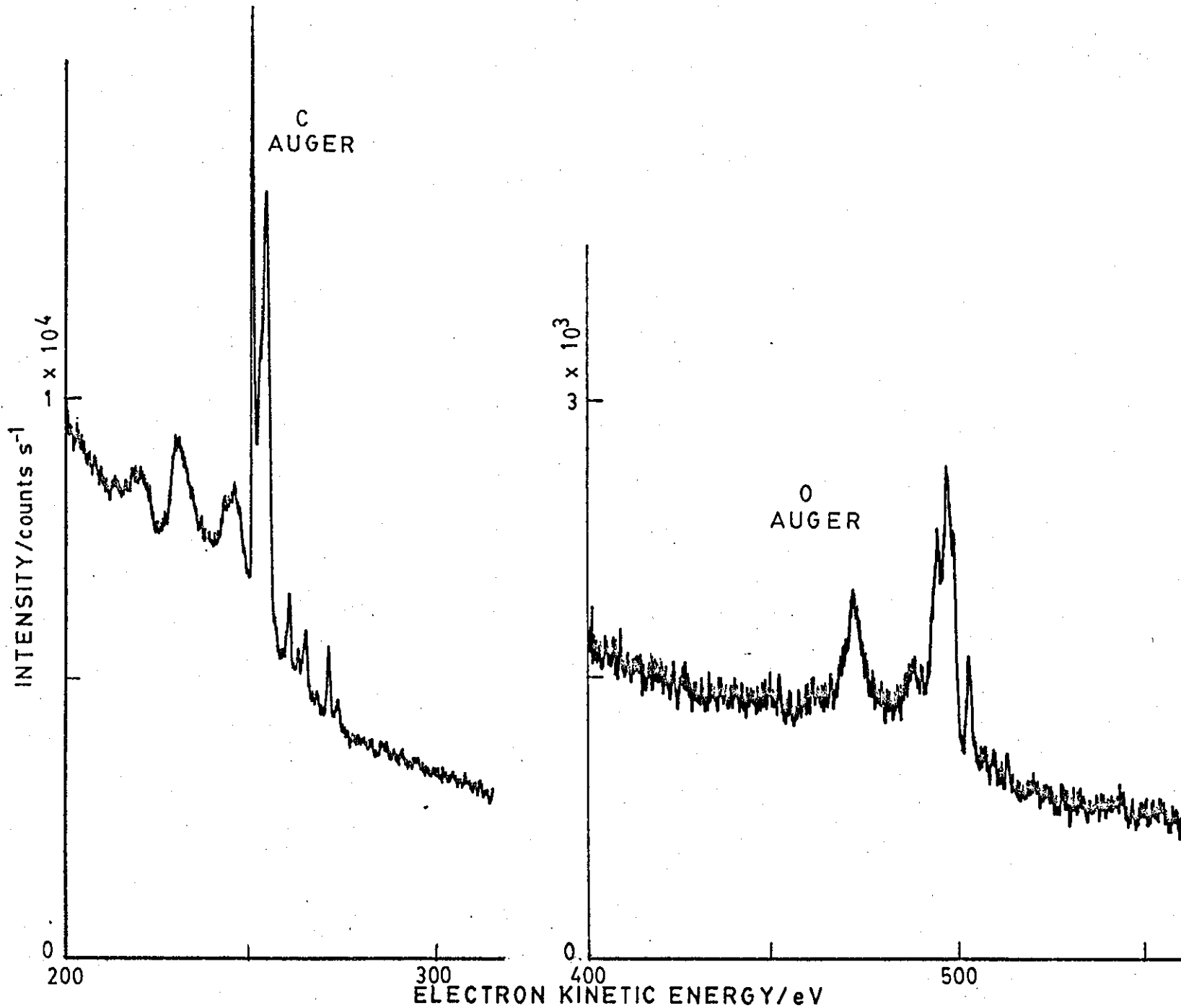
Date 18/5/78
Spectrum No. 1
Sample
       CO

     sam 10   t
Press ana   t
     gun 2×10^{-7} t

ENERGY SOURCE
Fil curr 3.4   A
Gun curr ~200 μA
Voltage   5 kV
X 2.72 Y 5.83 F 10
    Max Gun curr 189,

ANALYZER
Energy   50   V
Slits   20 mm

SCAN   C   O
Pedestal 200 / 400 V
Amplitude 300 / 300 V
Time   300 / 300 s
Counts 1×10^4 $3 \times 10^3 s^{-1}$
T.C. 0.33   s
Zero supp −
Exp x −

DETECTOR
Mult 3.2   kV
E Set 100
Mag trim −   mA

78

Fig. 4.8. Carbon and oxygen spectra of CO_2.
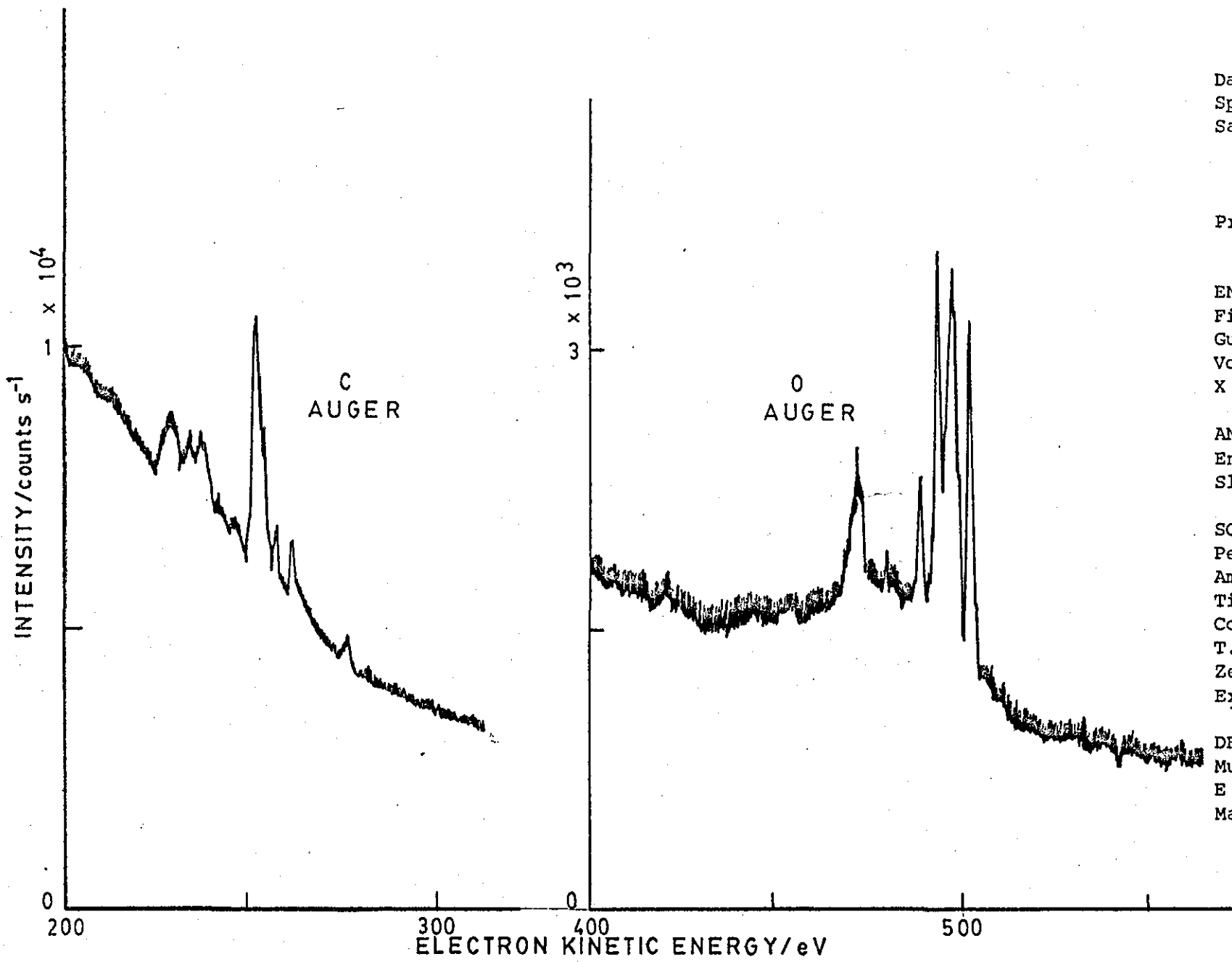
Date 16/5/78
Spectrum No. 3 ‡ 5
Sample

CO_2

sam 17		t
Press ana		t
gun 2×10^7		t

ENERGY SOURCE
Fil curr 3.4   A
Gun curr ~200   µA
Voltage   5   kV
X 2.73 Y 5.85 F 10
      Max gun curr 180µl

ANALYZER
Energy   50   V
Slits   2   mm

SCAN   C   O
Pedestal 200 |400 V
Amplitude 300| 300 V
Time   300| 300 s
Counts 1×10^4/3×10^3s-1
T.C.   0.33   s
Zero supp –
Exp x   –

DETECTOR
Mult 3.2   kV
E Set 100
Mag trim –   mA

79
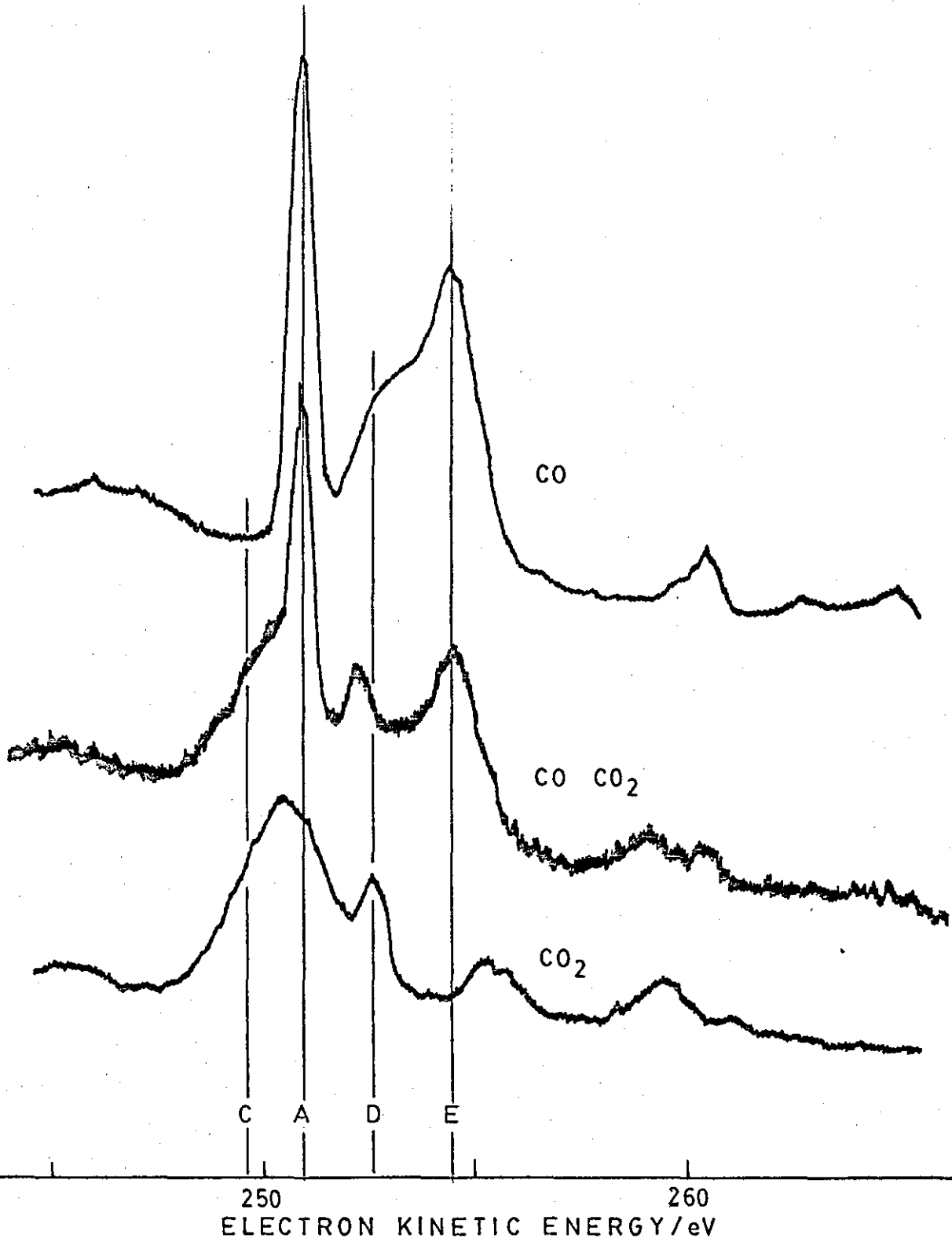
Fig. 4.9. Carbon Auger spectra of CO, CO_2, and a mixture of CO/CO_2. (Analyzer settings of 50 eV, 2 mm)
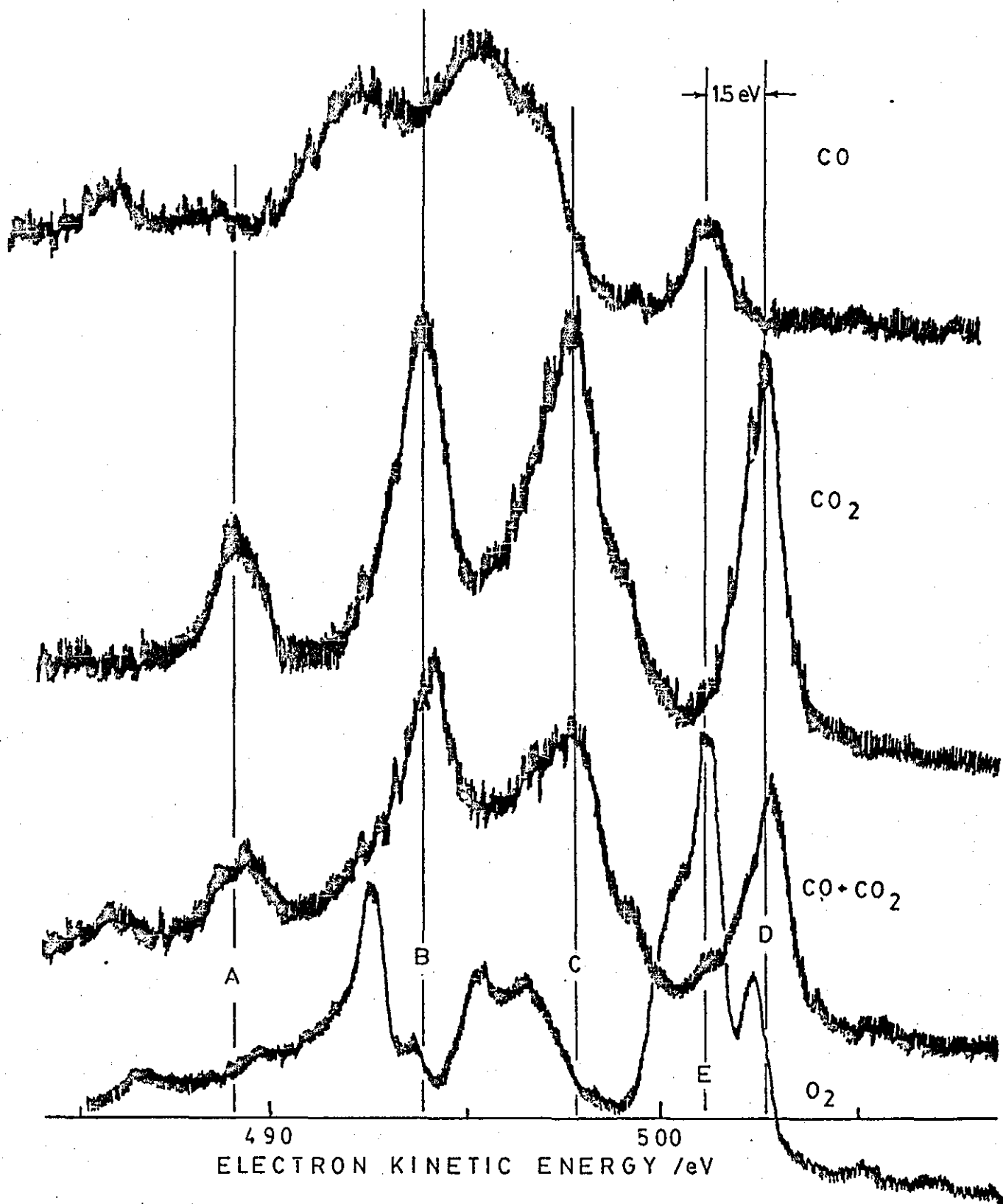
Fig. 4.10. Oxygen Auger spectra of CO, CO_2, CO + CO_2 and O_2.
(Analyzer settings of 50 eV, 2 mm)
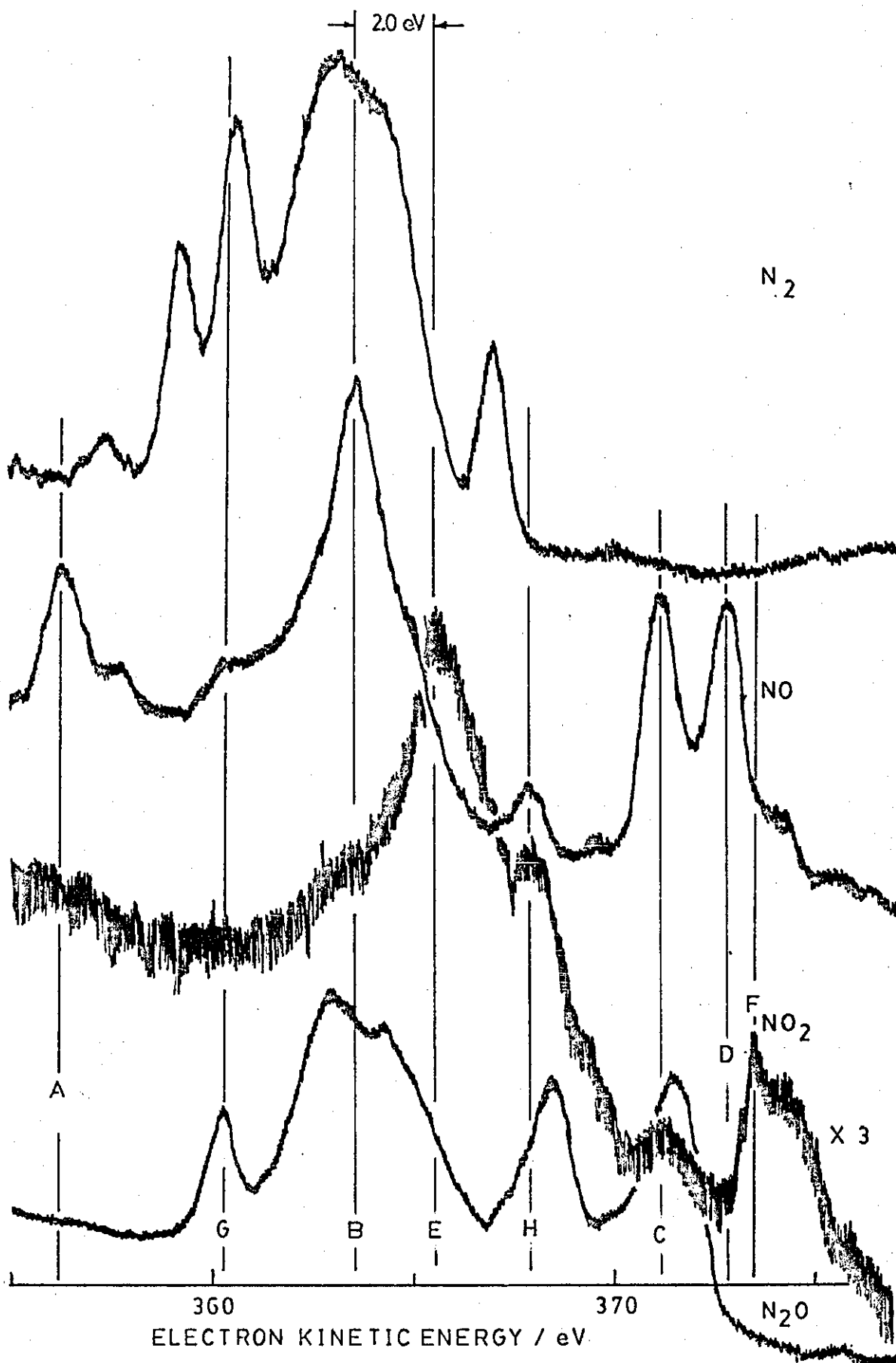
Fig. 4.11. Nitrogen Auger spectra of NO, NO_2, N_2O, and N_2.
(Analyzer settings of 50 eV and 2 mm)
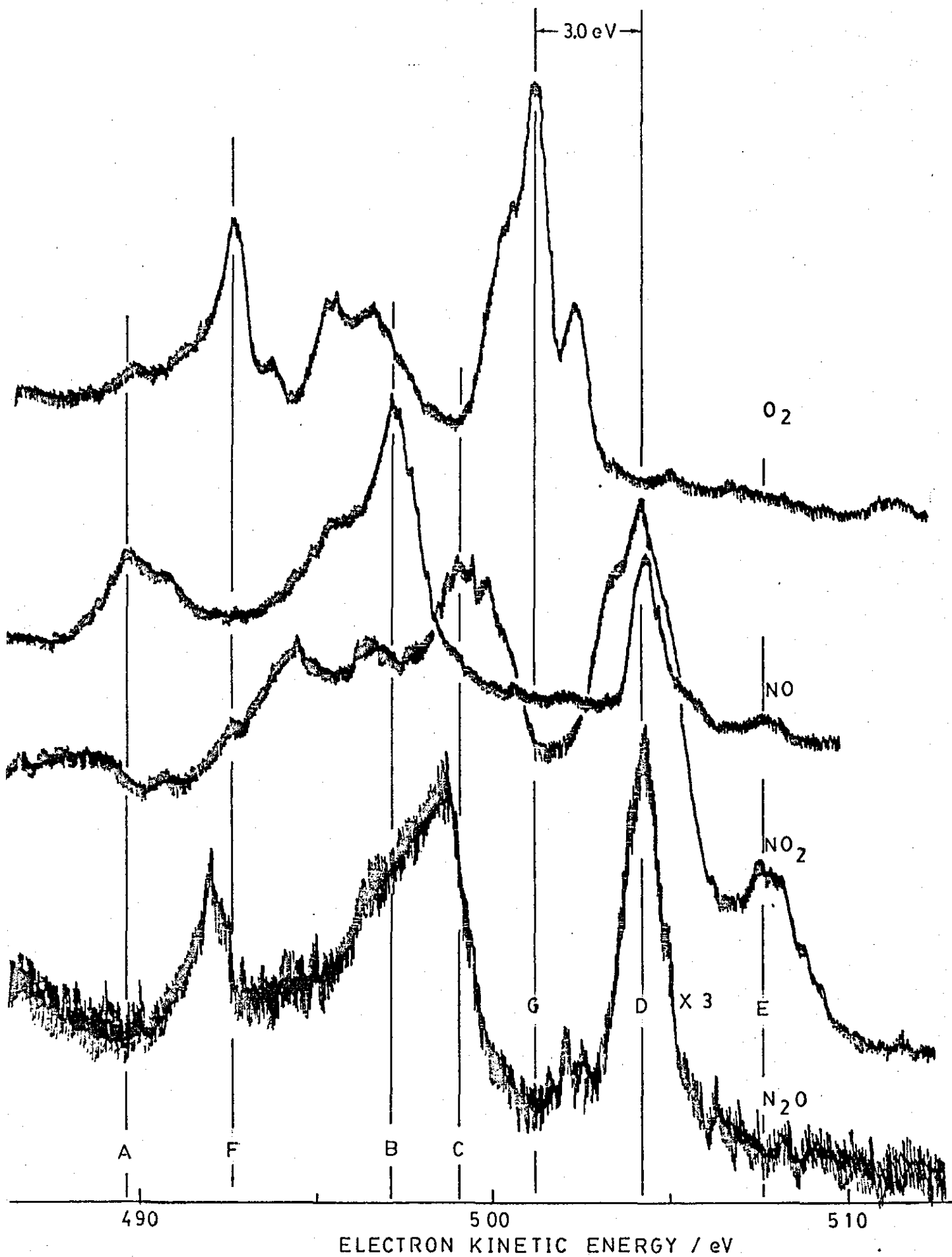
Fig. 4.12. Oxygen Auger spectra of NO, NO_2, N_2O, and O_2.
(Analyzer settings of 50 eV and 2 mm)
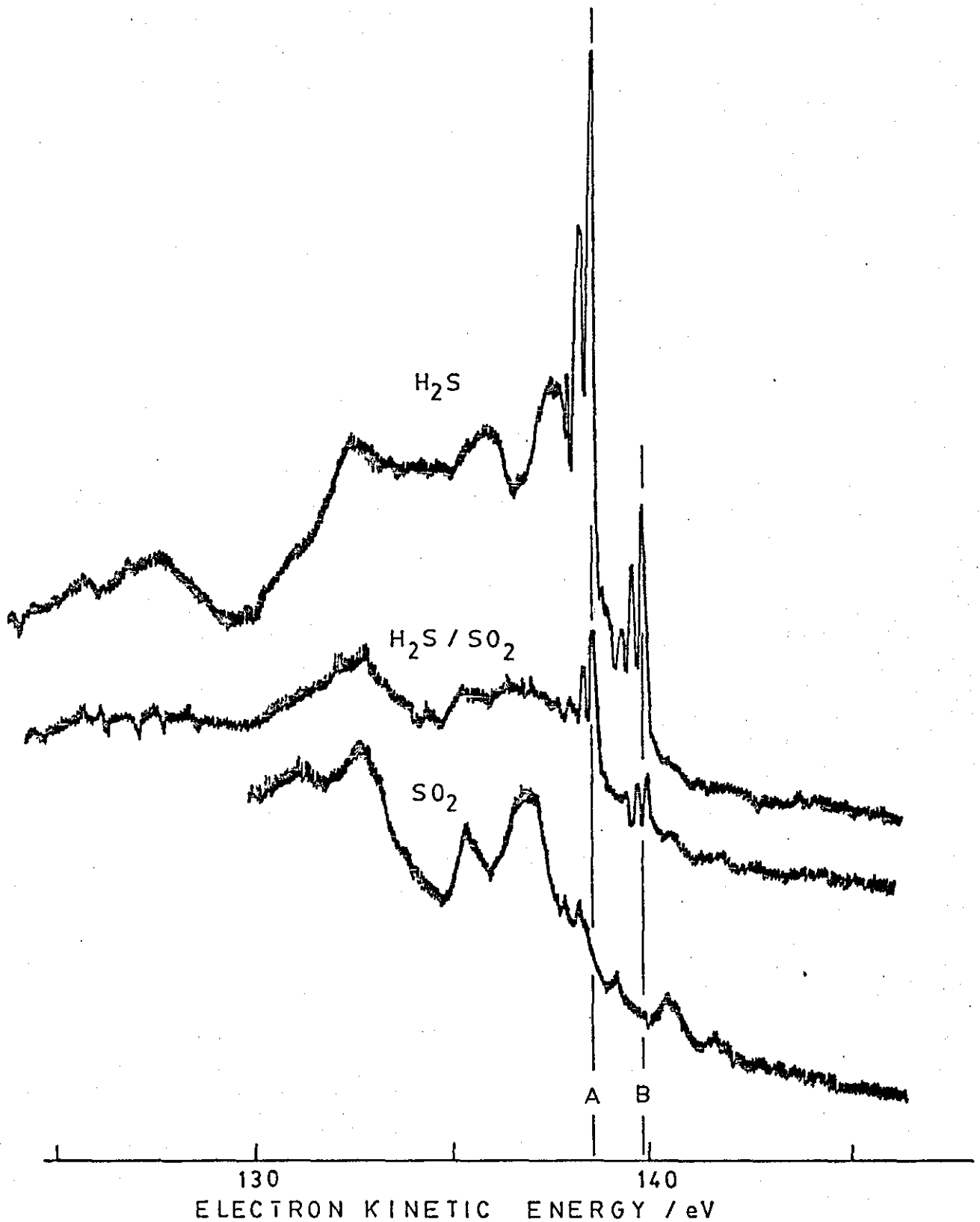
Fig. 4.13. Sulphur Auger spectra of H_2S, SO_2, and H_2S/SO_2 mixture. (Analyzer settings of 10 eV and 2 mm)

4.7.4. Analysis of H_2S and SO_2

The determination of the presence of SO_2 and H_2S in a mixture of both is an example of a situation simplified by a different elemental composition. Since only the SO_2 contains oxygen then its oxygen Auger spectra would be used for its identification. This is fortunate for this pair of compounds as the S spectra of SO_2 contains rather broad peaks and is less intense (detection limit is ca. two times greater, Table 5.4) than H_2S. The presence of hydrogen sulphide in a mixture can be detected by the presence of the peaks at A and B.

4.7.5. Summary

This chapter has briefly explained the Auger process, and the Auger spectrum and its analysis. The spectral interpretation method of Thompson et al. [2] was illustrated using CO, CF_4, and N_2 as examples. The method is useful, but is not complete in itself, for offering possible spectral interpretations.

The elemental analysis possibilities of AES for light elements in gases has been discussed. It has been shown (Figs. 4.5, 4.6) that C, N, O, F, Ne, S, Cl, and Ar could be detected without elemental spectral overlap.

Molecular analysis of gases and gas mixtures was also discussed. Examples illustrated were CO and CO_2, NO and NO_2, and H_2S and SO_2. The spectrum of a gas is very characteristic of the molecule and offers an easy method of identifying it. Mixtures of gases containing no common elements are also easily identified; however gases having common elements do have problem of spectral overlap. Components may, however, be determined under some circumstances.

Chapter 5

QUANTITATIVE ANALYSIS

5.1.   Introduction

This chapter deals with the quantitative aspects of the analytical potential of AES for gas analysis.

This is the first known systematic study of this topic. Therefore basic material such as nomenclature, errors, counting statistics, and the derivation of expressions for a figure of merit and limit of detection are included. Where possible this material is taken from related techniques, principally x-ray fluorescence spectrometry.

The limits of detection, sensitivity, and calibration curve functions are experimentally obtained for a number of atmospheric gases. Matrix effects and the linear range of the calibration functions are also considered. Experimental details are given as well as the description and operation of a purpose built gas sample preparation system.

5.2.   Nomenclature, Symbols, Units

    5.2.1.   General

In this section a compilation of many of the terms and symbols used in analytical AES is given. Some terms selected may eventually not prove to be the most appropriate but they will be used to provide consistency throughout this work. In many cases additional details of the individual terms are contained elsewhere in the report, therefore a minimal description only is included here. A glossary of these terms is given in Table 5.1.

A number of references [1 – 10] have been reviewed and the terms used in these have been compared. Those which seem to best agree with the rules established by the IUPAC [6,7,8] are in each case selected.

    5.2.2.   General Concepts

Measure of Concentration and Quantity

In AES, the quantitative measure is the intensity (I) of a selected Auger peak of the analyte. The concentration (c) or the quantity (q) of the analyte contained in the sample is derived from this observed measure. Random and systematic uncertainties in the value of I itself and its relationship to c and q determine the precision and accuracy of the analysis.

ELECTRON   KINETIC   ENERGY / eV
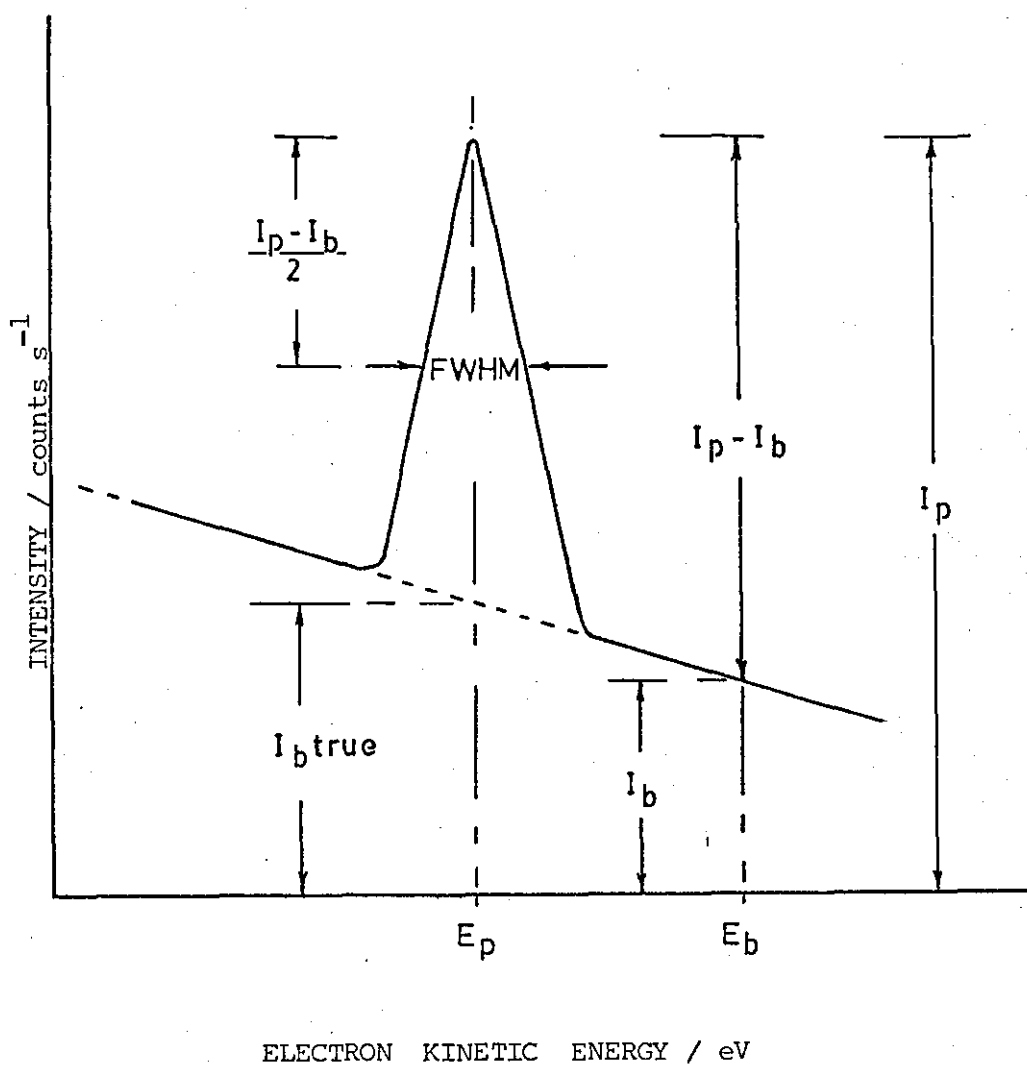
Fig. 5.1. Parameters used for analytical AES.

The analytical result is the final concentration or quantity of the element sought, after all subprocedures and evaluations have been performed. The analytical result is obtained from a measure of the analyte's Auger electron current intensity. The total signal measured is the peak intensity (I_p). The measure obtained when the background is measured is the background intensity (I_b). The difference ($I_p - I_b$) is called the net signal or intensity. The symbol S has been used for it but S is the recommended symbol for sensitivity; I_N might be a more appropriate symbol. The N referring to net. The electron kinetic energy at which I_p and I_b are measured are E_p and E_b respectively.

Sensitivity

The relationship between the intensity (I) of the signal and the analyte concentration (c) is given by the analytical curve. This curve is established by making measurements on a series of standards.

The sensitivity (S_i) for analyte i is defined as the slope of the analytical calibration curve. The sensitivity therefore is $(I_p - I_b)_i / c_i$ or q_i. S_i may vary with the magnitude of c_i or q_i; at low values of c_i or q_i, S_i is usually constant. S_i may also be a function of c or q of other analytes present in the sample.

$$S = (I_p - I_b) / \quad c \text{ or } q$$

$$c = (I_p - I_b) / S$$

$$\text{i.e. } c = I_N / S$$

CONCENTRATION (c) OR QUANTITY (q)
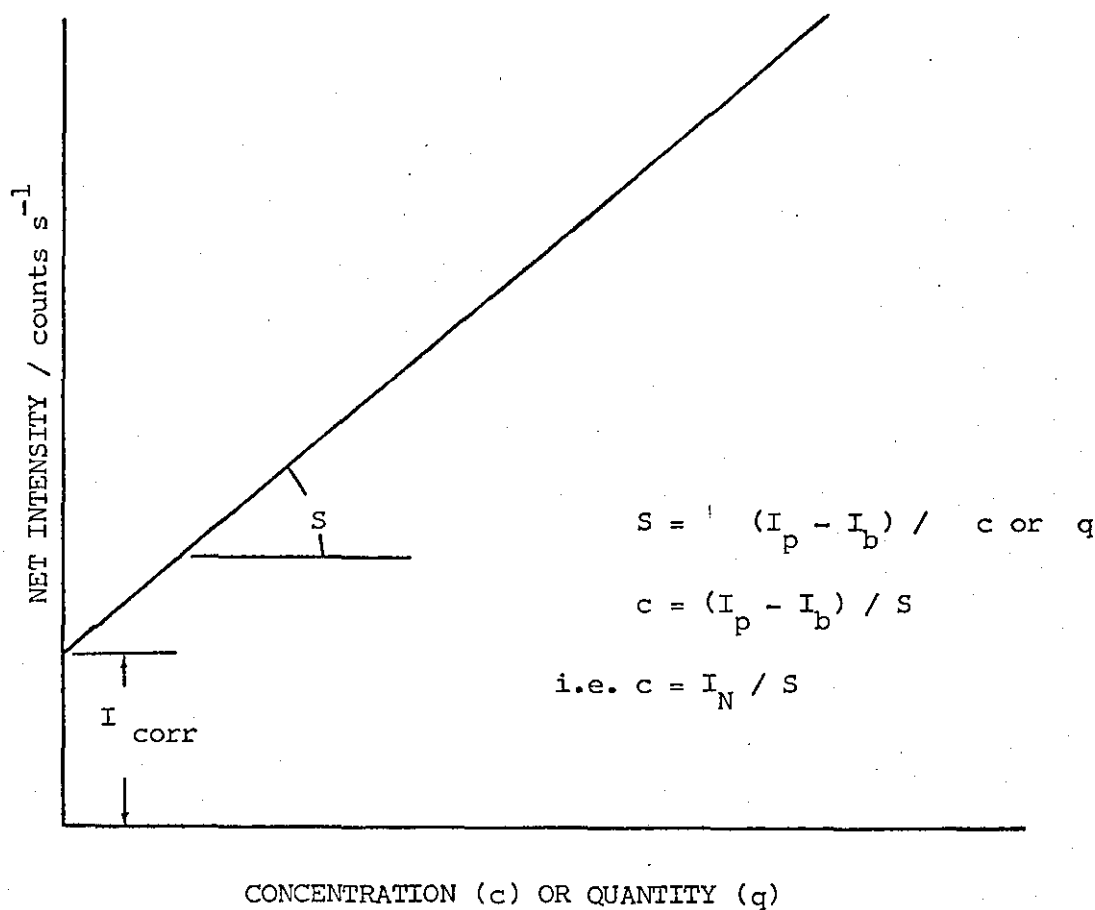
Fig. 5.2. Analytical calibration curve. If I_b true and I_b measured are not equal the calibration curve will not pass through the origin and hence $c = (I_p - I_b) / S$ has to be modified to $c = (I_p - (I_b + I_{corr})) / S$, where I_{corr} equals the difference between I_b true and I_b measured.

Statistical Terms

Terms such as standard deviation, relative standard deviation, variance, precision and accuracy have their standard definitions and usuage as outlined by the IUPAC.[6] One notable factor of Auger electron intensity is its random distribution. It follows a Poisson distribution, which in turn approximates a Gaussian distribution.

Therefore provided the number of counts is large and that no other counting error exists, then the standard deviation equals the square root of the number of counts i.e. $s = N^{\frac{1}{2}}$. This is covered more extensively in sec. 5.3.3.

Limit of Detection

The limit of detection, expressed as the concentration (c_L) or the quantity (q_L), is derived from the smallest intensity (I_L) that can be detected with reasonable certainty for a given analytical procedure. The expression used for the limit of detection is $3 / S_L \ (I_b / T_b)^{\frac{1}{2}}$ where T_b is the time used for counting the background. This expression is derived in sec. 5.4.

Figure of Merit

The expression used for figure of merit is also derived in sec. 5.4. It is $I_p^{\frac{1}{2}} - I_b^{\frac{1}{2}}$. The counting error will be at a minimum when the figure of merit is at a maximum.

Resolution

The resolution of the analyzer is the energy range (de) of the electrons passed by the hemispherical spectrometer. All electrons are retarded to the same energy by the potential difference applied between the collision chamber and the electrical centre point of the hemispheres. Therefore the resolution (de) is constant across any energy range examined. Tables 3.3 and 3.4 illustrate the resolutions available. The full width at half maximum is an experimental measure of the resolution; at high theoretical resolutions the experimentally determined FWHM tends to a constant value (sec. 3.2.2.). The alternate measure is percent resolution which is given by the following expression:

$$\frac{FWHM}{Peak\ Energy} \quad X\ 100\%$$

TABLE 5.1

TERMS AND SYMBOLS USED IN

ANALYTICAL AUGER ELECTRON SPECTROMETRY

Term	Symbol
Concentration, of element i	c, c_i
Quantity, of element i	q, q_i
Intensity (Measure of Signal, counts s^{-1})	I
for element i, average value	I_i; $\bar{I}$
peak intensity	I_p
background intensity	I_b
net intensity	$I_p - I_b$ $(=I_N)$
Time	T
Total counts $(I \times T)$	N
Standard deviation $(N^{\frac{1}{2}})$	s
Relative standard deviation	s_r
Auger electron energy, of peak	E_p
of background	E_b
Analytical calibration function	$I = g\,(c)$ or $I = g\,(q)$
Analytical evaluation function	$c = f\,(I)$ or $q = f\,(I)$
Sensitivity $(I\,/\,c)$	S
Limit of detection $(3/S\,(I_b\,/\,T_b)^{\frac{1}{2}})$	c_L, q_L
Figure of merit $(I_p^{\frac{1}{2}} - I_b^{\frac{1}{2}})$	FM
Signal – to – background ratio	$(I_p - I_b)\,/\,I_b$
Full width at half maximum	FWHM
Resolution	FWHM $/\,E_p$

5.3.   Errors in AES Analysis

5.3.1.   Types of Errors

Auger electron spectrometry of gases is a comparative technique and the accuracy of a measured result depends upon both the instrumental data and the calibration standards. The types and sources of the various errors in AES have been examined and estimates made of their magnitudes.

Errors of measurements are of three types; random, systematic and wild. The magnitude of the random error can be estimated by normal statistical procedures. Random errors result in the distri‑ bution of a number of results about the arithmetic mean of the mea‑ surement. Systematic errors result in the arithmetic mean of a measurement being different from the "true" result. Fig. 5.3 illustrates these two types of error. Both these error types are active in AES. Wild errors, resulting from mistakes such as typo‑ graphical errors, wrongly indentified samples, mis‑setting of the instrument etc. will not be considered further. To a first approxi‑ mation random errors limit precision, systematic errors limit accuracy.
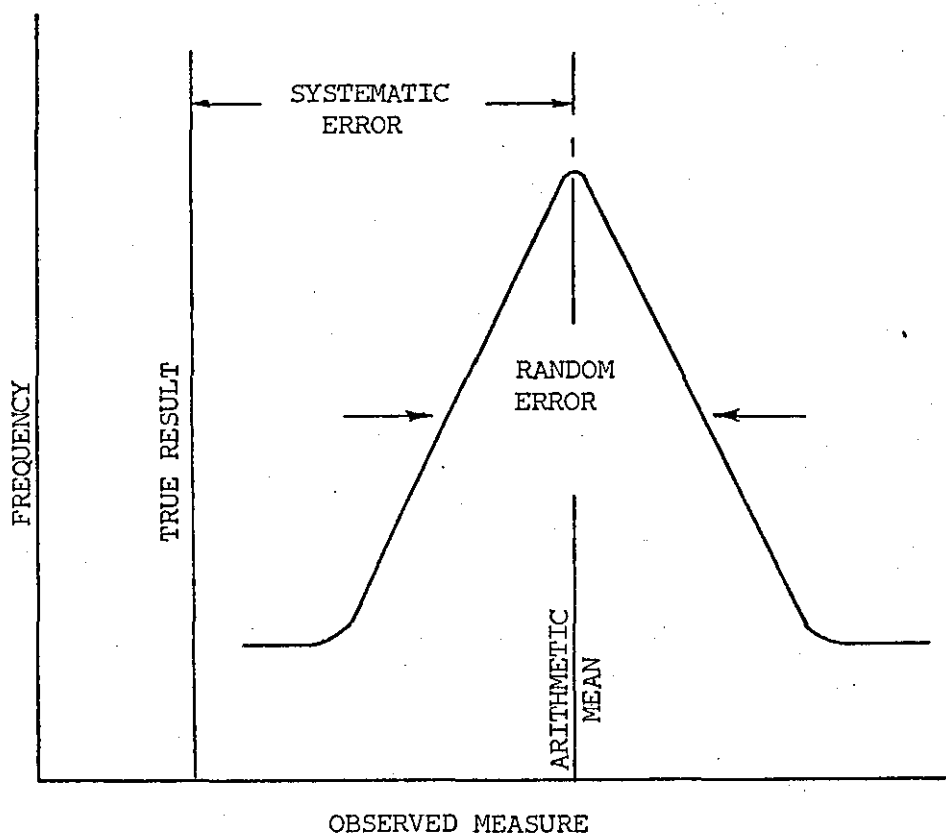
Fig. 5.3. Effect of random and systematic errors on precision and accuracy.

The errors may be classified by source as follows:

1. Statistical counting error (sec. 5.2.3) constitutes the best attainable precision and depends only on the total accumulated count.

2. Instrumental errors consist of short term and long term variation, instability, and drift in instrument components, conditions and parameters. These are principally the following:

– Electron gun potential and filament current.

– Intensity and distribution (focus) of the electron beam (caused by changes in dimension and position of internal components in the gun).

– Interaction of the sample gas with the electron gun filament.

– Interaction of the sample gas with the detector (not examined).

– Coincidence (dead time) losses in the detector and electronic circuitry.

– Electronic circuitry (drift in digital voltmeter etc.).

3. Operational errors (manipulative or resetting errors) consists of slight nonreproducibility in setting of instrument conditions. More minor errors would result from resetting the electron gun; filament current, the X and Y positions of the' electron beam, and the focus of the beam; and pulse height discrimator base line and detector potential. A major source of error is in resetting the sample gas pressure.

4. Specimen errors. These would include matrix effects, although these are expected to be minimal because of the low gas pressures used.

5. Error in estimation of concentration from the calibration curve.

6. Spectral line interference. A nearby spectral line can contribute to the intensity of an analyte line.

Counting errors, most instrumental errors, operational errors and errors in estimation of analyte concentrations from the calibration curve are random. Specimen errors, interaction of the sample gas with the electron gun and detector, and spectral line interference are systematic errors. Each of these errors may be expressed in terms of the standard deviation it contributes to the precision of the analytical result.

5.3.2. Random Errors

The major sources of random errors in Auger electron intensity measurements are those due to the equipment and to the random nature of Auger electron production, the latter being referred to as "counting statistics".

The main instrumental random error is that due to the electron exciting beam source. The electron gun has both a stabilized exciting beam current and exciting beam primary energy. As will be shown in sec. 5.5.2, the Auger current for a particular transition XYZ is dependent on both the exciting beam current and the exciting beam primary energy. From Figs. 3.2 and 3.3 it can be seen that the effect of random fluctuations in beam current and energy are dependent upon the actual values of each chosen. By choosing values on the plateaux of the relationships of Auger current vs. beam current and Auger current vs. beam energy the random fluctuations in Auger signal due to gun fluctuations can be minimized. The Model 301 electron gun has a beam energy stability of 0.002% hr^{-1} (i.e. $1 \times 10^{-8}\%$). The emission current stability is 0.02% $^{o}C^{-1}$ and 0.01% hr^{-1}.

As will be seen shortly the error due to counting statistics can be reduced by increasing the counting time. However instrumental errors will limit the minimum random error.

Because of the random distribution of Auger electrons the standard deviation (s) of a given number of collected electrons (N) is given by:

$$s = N^{\frac{1}{2}}$$

Therefore in an infinite series of measurements of N, having an arithmetic mean of $\bar{N}$, 63% would be between the limits of $\bar{N} + \bar{N}^{\frac{1}{2}}$ and similarly 92% (2s) would lie between the limits of $\bar{N} \pm 2\bar{N}^{\frac{1}{2}}$.

The fact that N fluctuates around $\bar{N}$ makes it possible to check whether these fluctuations are normal. Experimentally determined distributions of Auger electron measurements indicate that the short term distribution can be assumed to be normal.

5.3.3. Counting statistics

The random generation of Auger electrons like photoelectrons [2,11] and x-rays [9,10] follows a Poisson distribution. This distribution in turn approximates to a Gaussian distribution provided that the number of events is large. Therefore the error due to counting statistics is a truly random error and is found to obey the normal statistical rules for handling random events.

In general, the total random error will be dependant upon counting statistics, electron beam exciting source stability and other equipment errors. The total standard deviation of the random error is therefore

$$s_{total} = \sqrt{counting\ statistics\ variance + instrumental\ error\ variance}$$

Provided the instrumental error can be reduced sufficiently, and
that the systematic errors are negligible, the final precision of
the measurement can be predicted from the counting statistics.

It is often more useful to work with the relative standard
deviation or percent standard deviation.

$$s_r = s / N = N^{\frac{1}{2}} / N = 1 / N^{\frac{1}{2}} \qquad 5.1$$

$$s_r\% = 100 / N^{\frac{1}{2}} \qquad 5.2$$

Since the number of counts taken is the product of the counting rate
(I) and the counting time (T) therefore the relative standard devia-
tion is also given by:

$$s_r = 1 / (IT)^{\frac{1}{2}} \qquad 5.3$$

The background count rates are high in AES and must be taken
into account. The relative standard deviation of the net intensity
must therefore be used.

$$s = (s_p^2 + s_b^2)^{\frac{1}{2}} \qquad 5.4$$

$$= (N_p + N_b)^{\frac{1}{2}} \qquad 5.5$$

$$s_r = (N_p + N_b)^{\frac{1}{2}} / (N_p - N_b) \qquad 5.6$$

From equation 5.3 it can be seen that the relative standard
deviation of a measurement can be decreased by increasing the counting
time. Also from equation 5.3 it is obvious that the higher the signal
intensity the smaller the relative counting error will be. The
following table shows the standard and relative standard deviations
of the counting error for an increasing total number of counts. The
intensity (I) is 100 counts per second.

TABLE 5.2

VARIATION OF s AND s_r WITH COUNTING TIME

Number of counts* N	s** counts	s_r*** %	Counting Time T (s)
10	3.2	32	0.1
100	10	10	1
1,000	32	3.2	10
10,000	100	1.0	100
100,000	316	0.32	1,000
1,000,000	1,000	0.10	10,000

* $N = IT$

** $s = N^{\frac{1}{2}}$

*** s_r, % relative standard deviation $= 100 \, s \, / \, N$

Although the relative standard deviation of the counting error can be decreased with increased counting time there are practical limitations. The counting error is the limiting error only if the instrumental errors are negligable. As counting time increases extremely high stability is required for the current and potential of the exciting source, the detector, other readout components, and the sample pressure. Expirements have shown that for the existing Auger electron spectrometer there is considerable drift and therefore counting times should be kept low, 100 s or less.

Often it is the count rate (I) which is used rather than the total number of counts (N).

From equation 5.1

$$s_r (N) = s (N) / N$$

and

$$s_r (I) = s (I) / I \qquad\qquad 5.7$$

Therefore, for values of intensity and total count related to the same counting time (T) by $N = IT$, the relative standard deviations are equal, that is;

$$s_r = s (N) / N = s (I) / I \qquad\qquad 5.8$$

therefore from equation 5.3

$$s(I)/I = 1 / (IT)^{\frac{1}{2}}$$ 5.9

and

$$s(I) = I / (IT)^{\frac{1}{2}} = (I/T)^{\frac{1}{2}}$$ 5.10

Thus the relative standard deviation of the count rate equals $(IT)^{\frac{1}{2}}$.

It will be noted that equation 5.10 relates simply to the total counting rate (I), whereas, in practice AES requires the net counting error of the peak (I_p) and background (I_b) counting rates. The counting error can be calculated for three methods of counting. These are fixed count, fixed time, and optimal fixed time. The expressions [9] for the counting error are as follows:

Fixed Count: $I_p T_p = I_b T_b$ and $T_p + T_b = T$
(FC)

$$s_r = (1 / T^{\frac{1}{2}}) (I_p + I_b)^{\frac{1}{2}} (I_p / I_b + I_b / I_p)^{\frac{1}{2}}$$ 5.11

Fixed Time: $T_p = T_b = T / 2$ and $T_p + T_b = T$
(FT)

$$s_r = (2 / T)^{\frac{1}{2}} (I_p + I_b)^{\frac{1}{2}}) / (I_p - I_b)$$ 5.12

Optimal Fixed Time: $T_p / T_b = (I_p / I_b)^{\frac{1}{2}}$ and $T_p + T_b = T$
(OFT)

$$s_r = (1 / T^{\frac{1}{2}}) (1 / (I_p^{\frac{1}{2}} - I_b^{\frac{1}{2}}))$$ 5.13

Generally s_r (FC) $>$ s_r(FT) $>$ s_r(OFT), although in practice the fixed time method is easier to use.

5.4.   Figure of Merit and Limit of Detection

A consequence of equation 5.13 is that for a fixed analysis time, the net counting error will be a minimum when $I_p^{\frac{1}{2}} - I_b^{\frac{1}{2}}$ is at a maximum. It is this expression which has been used in chap. 3 for establishing optimum experimental conditions for quantitative analysis by AES. The other criteria used sometimes is the signal-to-background ratio, $(I_p - I_b) / I_b$. The following table illustrates that a higher signal-to-background ratio does not necessary give the minimum counting error.

TABLE 5.3

COMPARISON OF METHODS USING $I_p^{\frac{1}{2}} - I_b^{\frac{1}{2}}$ AND

SIGNAL—TO—BACKGROUND RATIO

Method	A	B	C
I_p	15,700	32,000	59,500
I_b	4,400	11,600	27,900
$I_p^{\frac{1}{2}} - I_b^{\frac{1}{2}}$	59	71	77
$s_r\%$ *	0.17	0.14	0.13
$(I_p - I_b) / I_b$	2.57	1.76	1.13

* optimal fixed time, $T = 100_s$

The limit of detection, expressed as concentration (c_L) is derived from the smallest intensity (I_L) that can be detected with a given certainty for a given analytical procedure. The value of I_L being given by the equation

$$I_L = I_b + Ks_b \qquad\qquad 5.14$$

Where I_b is the background intensity, s_b is the standard deviation of the background intensity and K is a numerical factor chosen according to the confidence level desired. IUPAC[6] recommends a K of 3. Although this normally would imply the 99.6% confidence level, in practice it probably is closer to a confidence level of about 90%. Each determination requires two intensity readings, I_p and I_b. This increases the error by $2^{\frac{1}{2}}$ and hence reduces the confidence level. i.e.

$s_{total} = (s_b^2 + s_p^2)^{\frac{1}{2}}$ but $s_b \approx s_p$ @ the detection limit $\therefore$

$$= (2s_b^2)^{\frac{1}{2}} = 2^{\frac{1}{2}} s_b$$

Since the analytical evaluation function is $c = I_N /S$ (Fig. 5.2), therefore the limit of detection is

$$c_L = Ks_b / S \qquad\qquad 5.15$$

in terms of intensity, since $s_b = (I_b / T_b)^{\frac{1}{2}}$ therefore

$$c_L = 3/S (I_b / T_b)^{\frac{1}{2}} \qquad\qquad 5.16$$

or in terms of net count, since $s_b = N_b^{\frac{1}{2}}$ therefore

$$c_L = (3/S) N_b^{\frac{1}{2}} \qquad\qquad 5.17$$

However in equation 5.16 S is dN / dc, therefore all samples and standards would have to be counted for the same length of time. In practice this could be inconvenient therefore equation 5.17 is to be preferred.

5.5. Sensitivity and Limits of Detection

5.5.1. General

Sensitivity in this study is defined as the rate of change of the net analyte line intensity with change in the amount of analyte, $S_i = (I_p - I_b) / c_i$ (sec. 5.2.2).

The limit of detection is defined as that amount of analyte that gives a net line intensity equal to three times the square root of the background intensity, or, in statistical terms, that amount that gives a net intensity equal to three times the standard counting error of the background intensity (secs. 5.2.2, 5.4).

$$c_L = 3 / S_i (I_b / T_b)^{\frac{1}{2}}$$

So many factors affect the sensitivity that a given value applies only for the specified sample and instrument conditions. The limit of detection is likewise dependent on the same conditions.

5.5.2. Factors Affecting Sensitivity and Limit of Detection

Two equations which indicate some of the factors affecting the sensitivity and limit of detection are:

$$I_A = I_p \cdot G \cdot P \cdot r (E_p, P) \cdot \phi (E_p, E_x) \cdot \gamma_{xyz} \cdot S (E_{xyz}, P) \qquad (12)$$

and

$$c_L = 3 / S_i (I_b / T_b)^{\frac{1}{2}} \qquad \text{(secs. 5.2.2, 5.4)}$$

The Auger current (I_A) and hence the sensitivity are dependent on : the electron gun beam current (I_p) and beam energy (E_p); the efficiency of the spectrometer in collecting the Auger electrons (G); Auger transitions caused by scattered electrons (r (E_p, P); the cross section for ionization of level X of binding energy E_x by an electron of energy E_p $(\phi(E_p, E_x))$, and the probability of relaxation by the Auger transition XYZ following

ionization of X (γ_{xyz}) of the particular analyte; and the sample pressure (P) which also affects the probability (S) of Auger electrons of energy E_{xyz} escaping without an inelastic gas-electron collision. The terms I_A, I_p, and S are not to be confused with those used in Table 5.1.

The limit of detection is therefore also affected by the above factors since they affect the sensitivity. It is also dependent on the counting time. These factors and others were experimentally studied. The results of these studies are given in chapter 3.

5.5.3. Experimental

Reagents

Most of the gases studied in this work were of reagent purity (British Oxygen Co. Ltd., Matheson Gas Products) and were used without further purification. The nitrogen dioxide was prepared by reacting nitric oxide and oxygen and was then purified by repeated condensations and degassings in a dry ice-acetone bath.

Equipment

The equipment used was the Vacuum Generators AFM2 Auger electron spectrometer, a Nuclear Enterprises Ltd. Scaler − Rate meter (SR5) and the sample preparation system (sec. 5.6).

Procedures

Four gas mixtures were prepared using the procedure outlined in sec. 5.6.2. These gas standards contained 0, 5, 10, and 20 mol % of the analyte in the dilutant gas. Nitrogen was the dilutant gas, except for nitrogen and the nitrogen oxides where argon was used, and for sulfur dioxide where acetylene was used.

The instrumental conditions used were as follows:

	sample expansion chamber	10 − 15 torr
Pressures	analyzer chamber	ca. 1.5×10^{-5} torr
	electron gun stack	4.0×10^{-7} torr
	filament current	ca. 3.2 A
Electron Gun	beam current	200 uA
	beam voltage	4 or 5 kV
Analyzer	energy	50 eV
	slit	2 mm

Counting Time   10s

Detector   multiplier voltage   3.2 kV

                    E setting   100/1000

Some samples were also run at an electron gun stack pressure of 2×10^{-7} torr and/or an electron gun beam current of 100 µA.

The spectrum of the most concentrated standard was first obtained and from it the energy of the most intense peak was determined, i.e. E_p. Next a background energy, E_b was selected. It was E_p + 5, 10 or 15 volts, usually +5 volts if suitable. The analyzer voltage can be changed in steps of 5 volts. Each standard was then counted.

The sample container was attached to the new sample introduction system, i.e. valve 23. Valve 23 was opened and the space between the valve 23 and the valve of the sample container was evacuated. Valve 23 was then closed, the sample container valve opened and then closed. Again the space was evacuated. This was repeated three times to ensure that the previous sample was flushed from the sample expansion chamber. The sample chamber was then filled to a pressure of 10 – 15 torr.

The pressures and instrumental conditions were set to those previously noted. These conditions were maintained for 10 minutes to allow the intensity output to stabilize (sec. 5.7). The analyzer voltage was set to E_p and a 10s count of the peak intensity (I_p) measured on the scaler-timer. The analyzer voltage was then stepped to E_b, the sample pressure readjusted if necessary, and a 10s count of the background intensity (I_b) measured. Each measurement was then repeated.

5.5.4. Results and Discussion

The concentration and the net intensity (I_p – I_b) were calculated for each sample (Fig. 5.4). Then, the analytical calibration curve of net intensity vs. mol % of analyte was drawn. Figs. 5.5 to 5.10 show examples of these; the error shown is +/– two standard deviations of the net counting error (equation 5.12). It was necessary to plot the net intensity as the peak intensity varied greatly, this would seem to be due to fluctuations in the background. Due to the sloping background signal it was not possible to find an E_b at which the true and the measured background intensity were equal. E_b was always at a higher energy than E_p, and I_b (measured) was therefore lower that I_b (true). This resulted in

Sample No.	CO_2 Press cm Hg	Total Press cm Hg	Mol % CO_2	$\underline{CO_2}$ E_p = 502.6 eV E_b = 507.5 eV $I_p - I_b$** counts s^{-1}		$\underline{CO_2}$ E_p = 250.3 eV E_b = 265.1 eV $I_p - I_b$** counts s^{-1}		Sensitivity and Limit of Detection
1			0	12064.7 10755.0 1309.7	11852.3 10567.4 1284.9	1761.5 1713.4 48.1	1766.3 1730.4 35.9	$\underline{C \ in \ CO_2}$ S = 138.8 c/s/% I_b = 12000 c/s $c_L = \dfrac{3}{138.8} \dfrac{\sqrt{12000}}{100}$ = 0.2368 mol %
2	31.80* 29.30* 2.50	36.10* 28.70* 57.40	$\dfrac{2.50}{57.40} \times 100$ = 4.36	12676.2 10638.4 2037.8	12807.1 10670.4 2136.7	2110.4 1798.1 312.3	2163.8 1817.3 346.5	
3	35.20* 29.30* 5.90	33.90* 28.70* 55.20	10.69	13224.0 10212.4 3011.6	12916.2 9939.6 2976.6	2585.3 1863.8 721.5	2593.8 1828.2 765.6	$\underline{O \ in \ CO_2}$ S = 65.04 c/s/% I_b = 1760 c/s $c_L = \dfrac{3}{65.04} \dfrac{\sqrt{1760}}{100}$ = 0.1935 mol %
4	40.30* 29.25* 11.05	41.55* 28.65* 62.90	17.57	14278.3 10782.5 3495.8	13928.3 9916.4 4011.9	3169.5 2037.3 1132.2	3268.1 2031.2 1236.9	

* Manometer readings

** Duplicate readings

Fig. 5.4. Typical calculation of sensitivity and limit of detection. Data for carbon and oxygen of carbon dioxide.
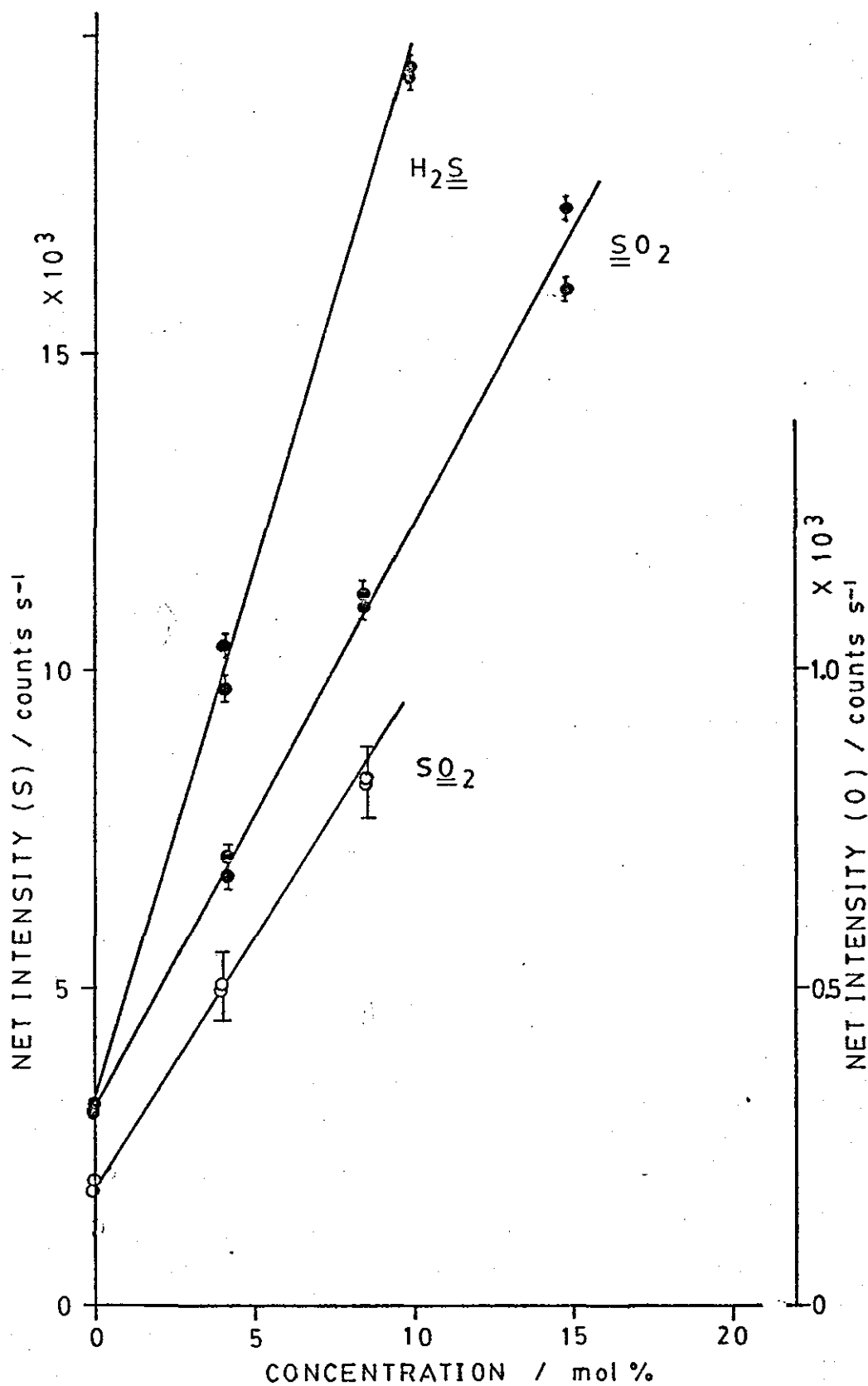
Fig. 5.5. The AES analytical calibration curves for the S of H$_2$S and the S and O of SO$_2$. Counting errors are +/- 2s, calculated using Equation 5.12.
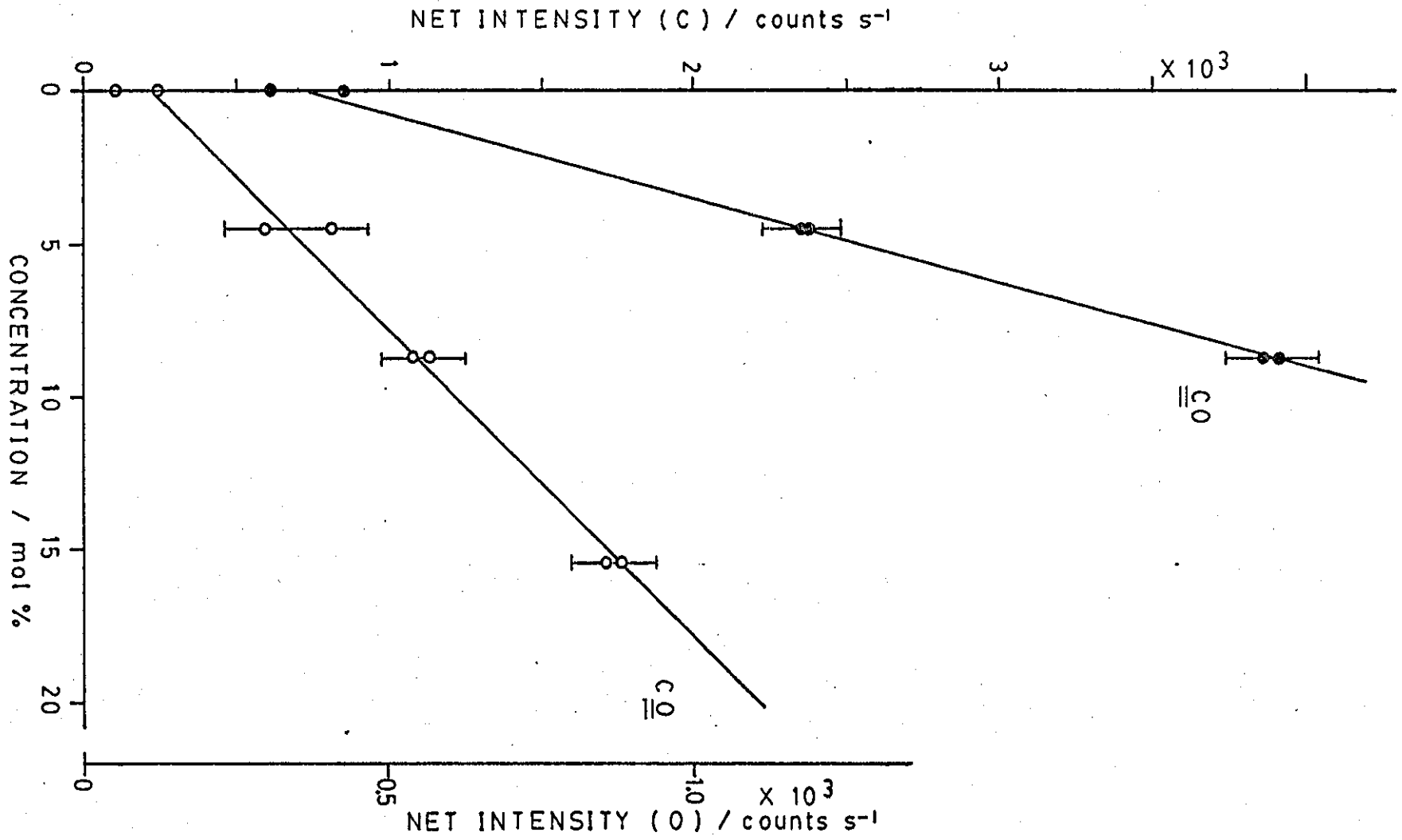
Fig. 5.6. The AES analytical calibration curves for the C and O of CO.
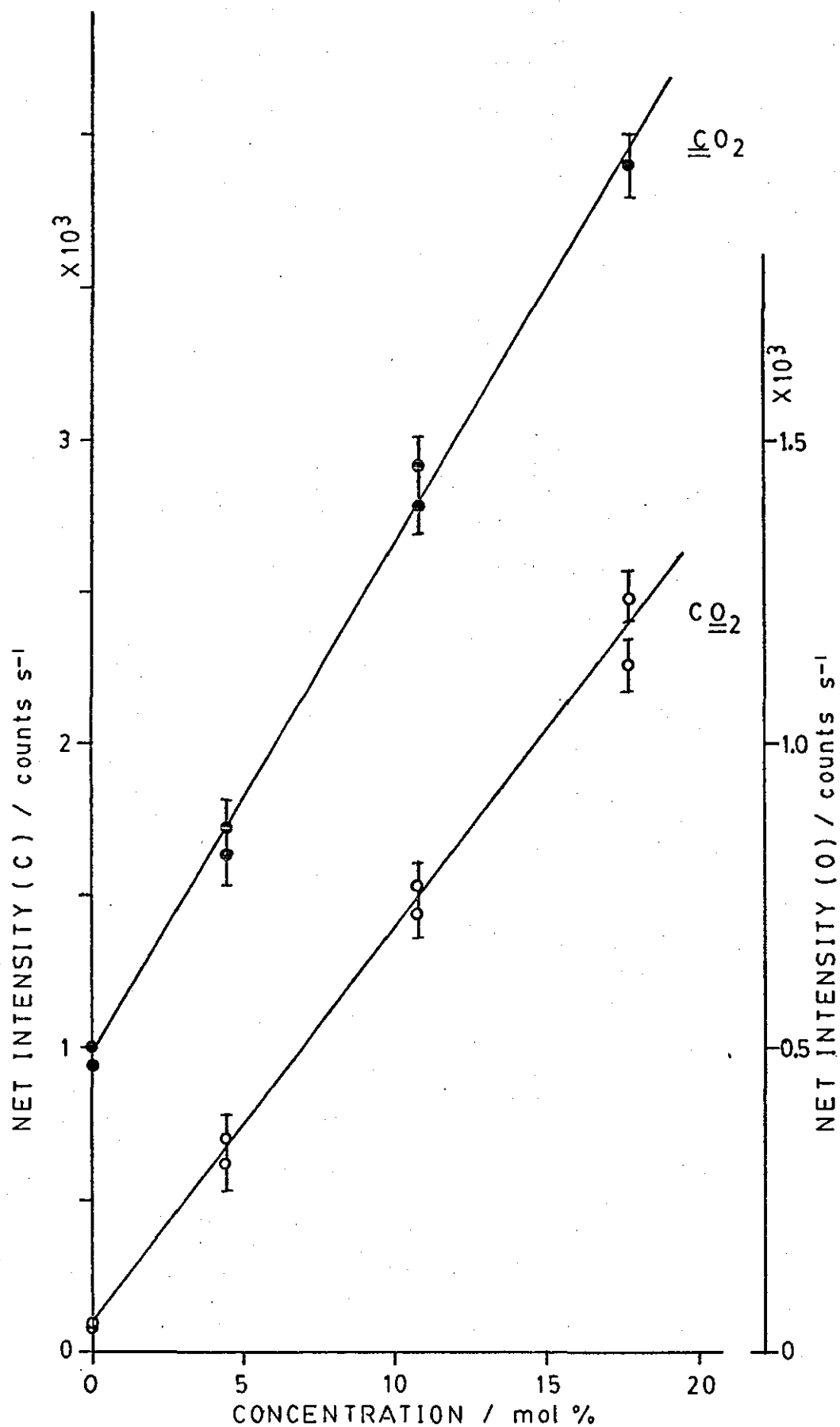
Fig. 5.7. The AES analytical calibration curves for the
C and O of CO_2.
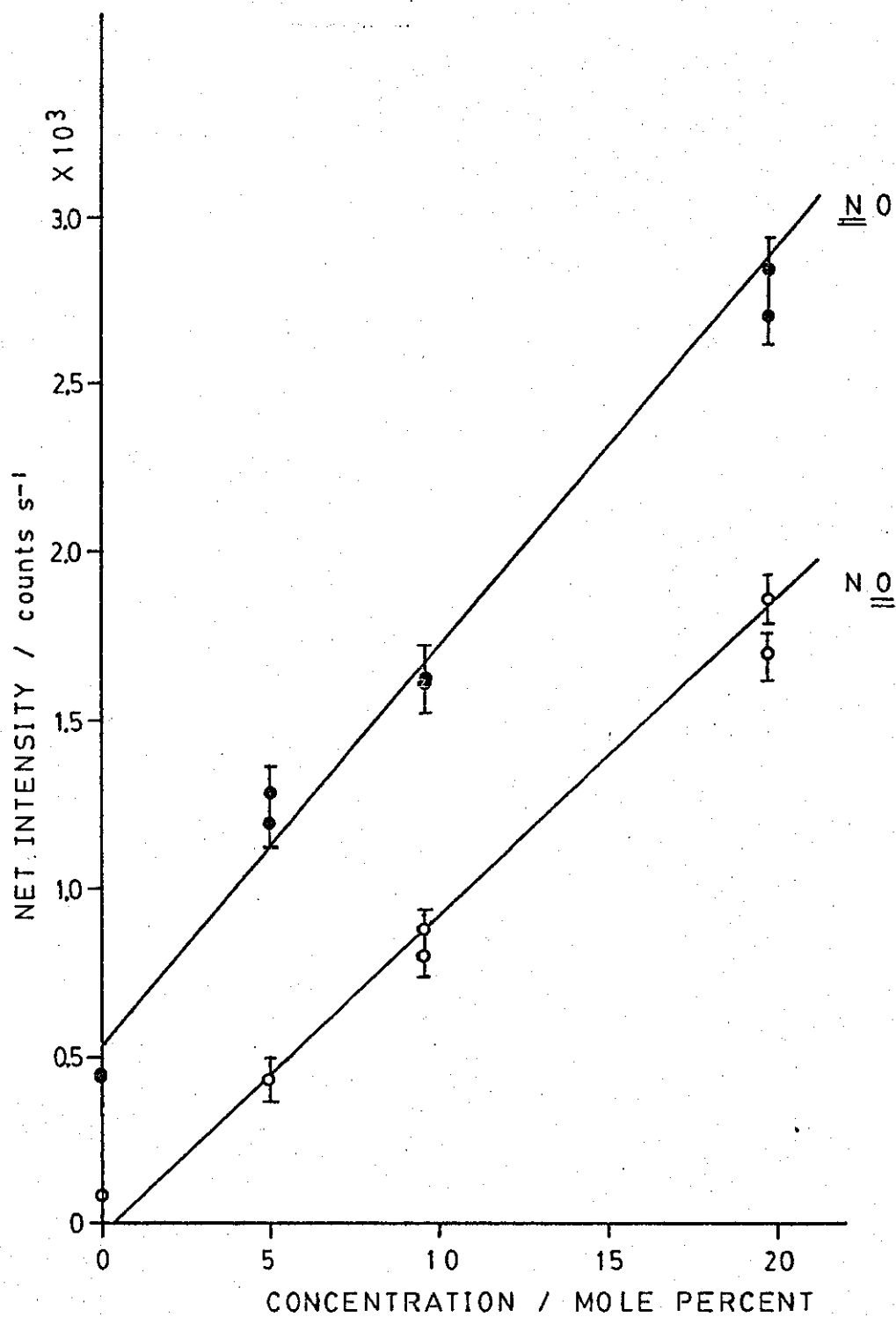
Fig. 5.8. The AES analytical calibration curves for the N and O of NO.
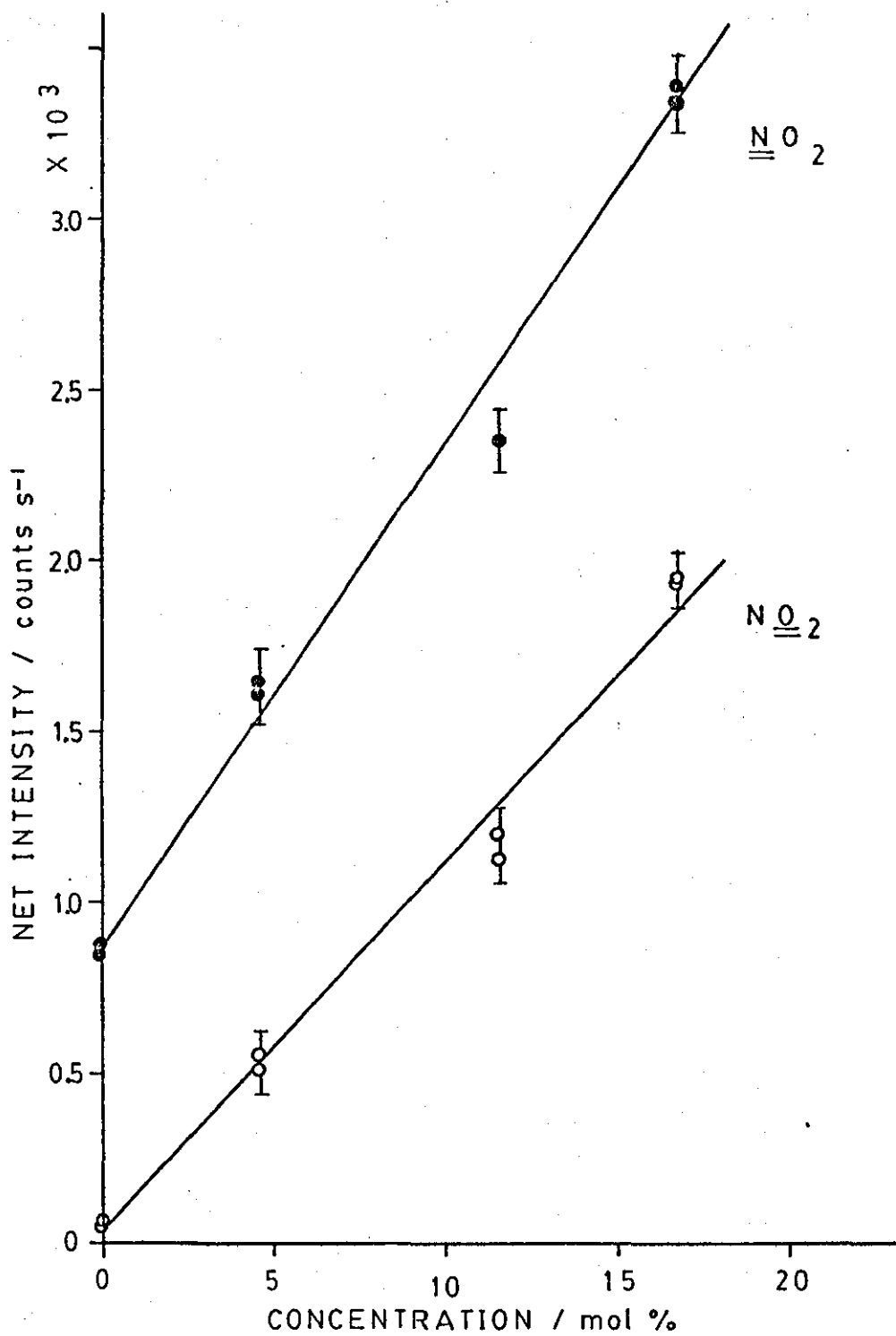
Fig. 5.9. The AES analytical calibration curves for the N and O of NO_2.
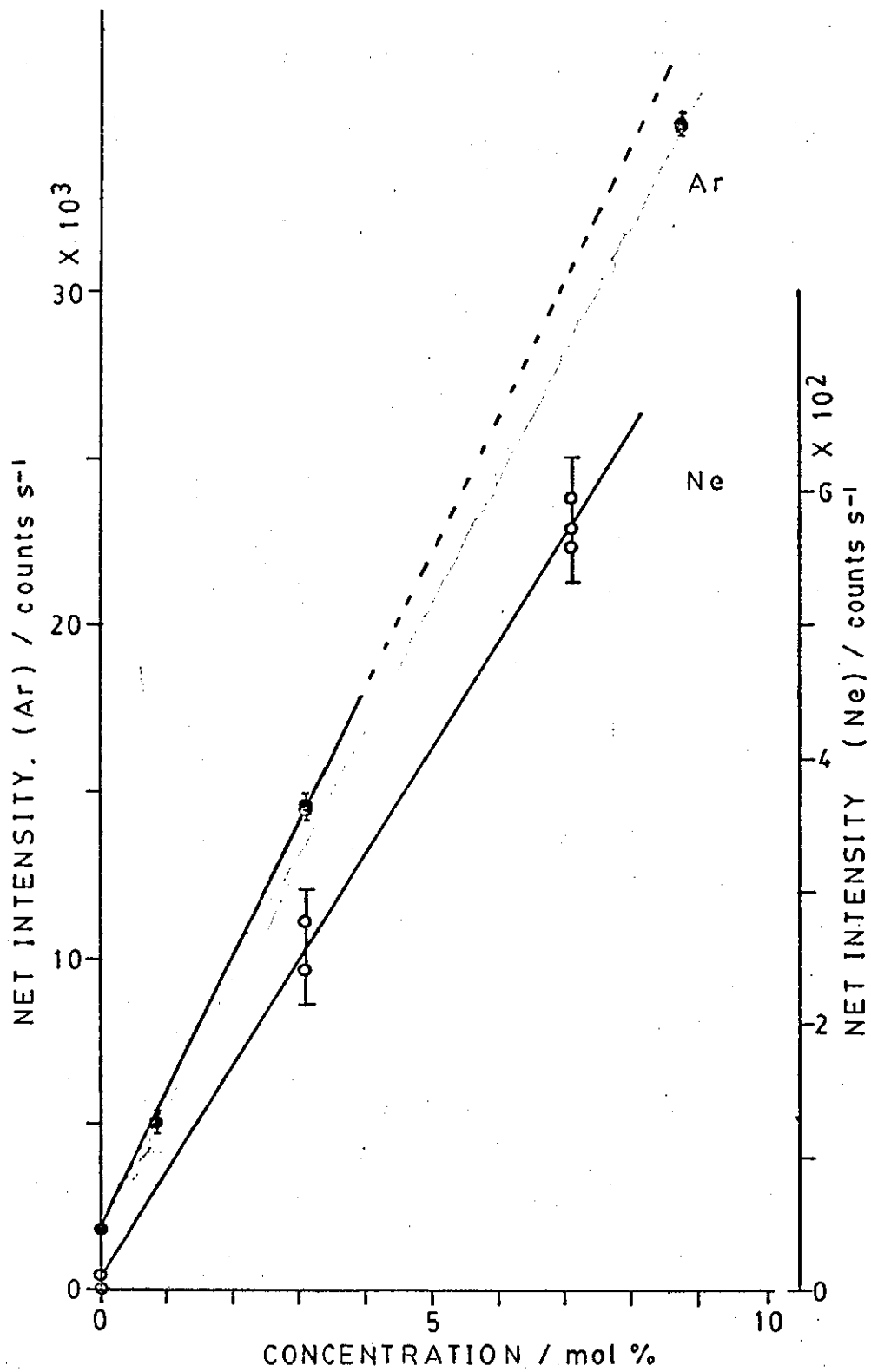
Fig. 5.10. The AES analytical calibration curves for the inert gases Ar and Ne.

calibration curves which did not go through the origin.

The calibration curves were then examined to determine their linear range. Many were linear over the full range, some however were linear only over a range of 0 to 10 mol % or less. This is probably due to high count rates and the dead time loss of the detector and/or circuits. Maximum count rates should be limited to about 30,000 counts s^{-1} to obtain linear calibration curves. An approximate dead time (resolution time) for the overall counting system was calculated from the analytical calibration curves of argon (Fig. 5.10) as well as H_2S and SO_2 curves (not shown). This dead time was 0.7 to 0.8 μs, it was probably low due to the approximation method used. Assuming a dead time of 1 μs the count loss at 30, 40, and 50 thousand counts per second (measured) would be 0.9, 1.7, and 2.6 thousand counts per second.

The slope of the linear portion of the calibration curve was then calculated by linear regression. This slope was the sensitivity in terms of counts per second per mol %.

The background intensity was estimated from the values of I_p for the blank. The detection limit (c_L) was then calculated using

$$c_L = 3 / S \, (I_b / 100)^{\frac{1}{2}}$$

where 100s was used as the arbitrarily chosen count time. Sensitivities and limits of detection are listed in Tables 5.4 and 5.5.

For the elements C, O, N, and Ne the limits of detection vary between 0.1 and 0.4 mol %, sulphur varies between 0.04 and 0.07, and argon has a detection limit of 0.01 mol %.

AES does have a capability for analyzing gas samples where spectral overlap is not a problem. Matrix absorption is minimal (sec. 5.7) and, assuming total count rates of approximately 30,000 counts s^{-1} or less, linear or near linear analytical calibration curves should be obtained for any concentration range. Although limits of detection of less than one half mol % have been calculated a detection limit and reproducibility limit of ca. one mol % would be more realistic for routine work.

TABLE 5.4

SENSITIVITIES AND LIMITS OF DETECTION*

FOR AUGER ELECTRON SPECTROMETRIC

ANALYSIS OF GASES

ELEMENT	COMPOUND	SENSITIVITY counts s^{-1}mol%$^{-1}$	I_b, counts s^{-1}	LIMIT OF DETECTION		E_p, eV	E_b, eV	Max. Beam current μA
				Mol %	vpm			
N	NO	119	16,000	.3200	3200	364.1	369.0	450
O	NO	94	10,000	.3250	3250	497.0	501.9	
N	NO$_2$	145	11,700	.2240	2240	365.9	380.7	450
O	NO$_2$	109	6,800	.2270	2270	504.2	509.0	
C	CO	360	19,500	.1170	1170	251.3	255.2	600
O	CO	50	4,400	.4000	4000	495.2	504.7	
C	CO$_2$	168	9,600	.1750	1750	250.3	265.1	220
O	CO$_2$	65	1,760	.1940	1940	502.6	507.5	
C	C$_2$H$_2$	201	10,000	.1490	1490	257.0	261.9	225
S	H$_2$S	1650	39,000	.0360	360	138.8	143.6	220
S	SO$_2$	935	45,500	.0684	684	137.1	141.9	600
O	SO$_2$	79	2,800	.2010	2010	498.5	508.3	600
Ar	Ar	4130	22,300	.0110	110	204.1	209.0	230
Ne	Ne	80	7,000	.1000	1000	804.8	809.6	240

* Conditions of analysis as outlined in sec. 5.6.3.

TABLE 5.5

SENSITIVITIES AND LIMITS OF DETECTION*

FOR AUGER ELECTRON SPECTROMETRIC

ANALYSIS OF GASES

ELEMENT	COMPOUND	SENSITIVITY counts s^{-1} mol $\%^{-1}$	I_b, counts s^{-1}	Limit of Detection, vpm	E_p, eV	E_b, eV	Beam current μA	Gas pressure $\times 10^{-7}$ torr	Max. beam current, μA
C	CO	335	11,200	948			100	4	240
C	CO	132	6,900	1880			100	4	150
O	CO	16	1,300	6650			100	4	150
C	CO_2	139	12,000	2370			200	2	
O	CO_2	37	1,100	2680			200	2	220
C	C_2H_2	119	6,300	2000			200	2	225
C	C_2H_2	80	80	3340			100	2	180
S	H_2S	1000	26,000	480			200	2	220
S	SO_2	620	37,500	940			200	4	
S	SO_2	465	25,000	1020			200	2	200
S	SO_2	498	16,600	956			100	4	600
O	SO_2	36	860	3480			100	4	600
Ar	Ar	2800	12,200	123			200	2	250
N	N_2	60	2,600	2560			200	2	260
N	N_2	78	2,500	1920	363.6	368.5	100	4	160
N	N_2	45	1,500	2590	363.6	368.5	100	2	160
N	N_2O	33	2,050	4120	371.5	376.4	100	4	180
O	N_2O	14	1,000	6980	504.1	509.0	100	4	180
N	NH_3	30	2,400	4840	364.4	379.2	100	4	175
N	NH_3	15	1,420	7480			100	2	175
O	O_2	66	1,360	1670	500.7	505.6	100	4	160
O	O_2	36	820	2380			100	2	160

* Conditions of analysis as outlined in sec. 5.6.3. except for beam currents and gas pressures as noted in the table.

Fig. 5.11. Gas mixture preparation system.
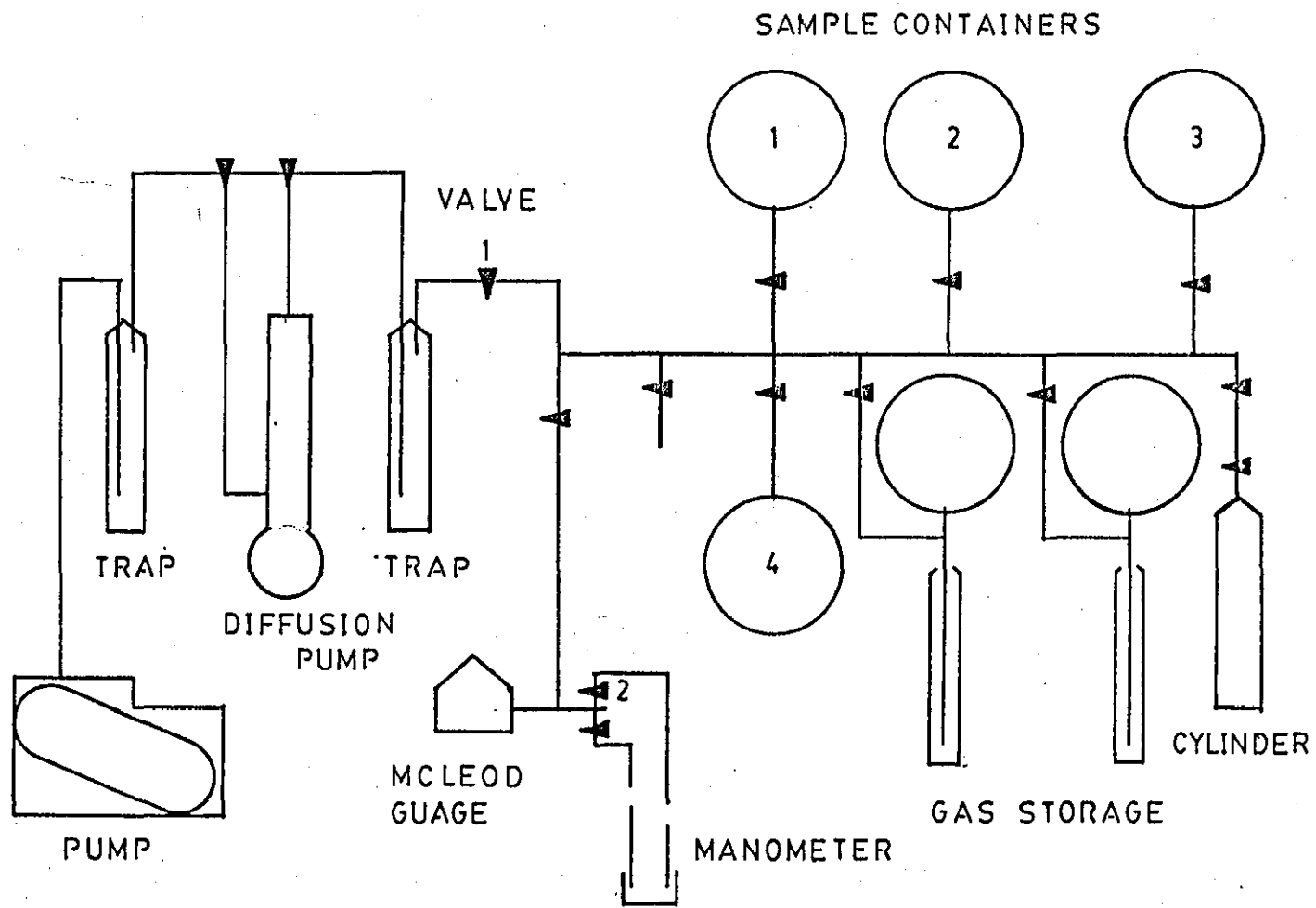
5.6.   Sample Preparation and Introduction System

5.6.1.   General

The AFM2 spectrometer can be presented with gaseous, liquid, or solid samples. In this study only gaseous samples were used. Liquid samples analyzed were first vaporized outside the spectrometer.

The original design of the instrument for admission of gaseous samples and the preparation of gaseous samples (ex. analyte plus dilutant gas) was both awkward and inexact. Therefore a sample preparation system was built (Fig. 5.11). All gas mixtures analyzed were prepared in this apparatus. The method of introducing the sample into the spectrometer was also altered (sec. 2.2.1) to improve the ease of operation and to insure no air leakage into the sample.

Sample concentrations were calculated using the ideal gas law, PV = nRT. Assuming the temperature is the same for all components, then $n_i \propto P_i v_i$. Each sample is prepared in one container, therefore the volume (V_i) is the same for all components. The quantity (n_i) of each gas in a sample is therefore proportional to its partial pressure (P_i). Concentration is expressed as mole fraction, mole percent or vapour parts per million. Mole percent (mol.%) and vapour part per million (vpm = mol % x 10^4) are both used in this study. The concentration is calculated from the partial pressure of the component and the total gas pressure of the sample.

Mol % = P_i / P_t X 100

5.6.2.   The Sample Preparation System

The system consists of a rotary vacuum pump, mercury diffusion pump, mercury manometer, miniature McLeod gauge, gas storage containers, gas inlet valve and up to five sample containers. It is adequate to conveniently produce simple gas mixtures; mixtures of up to three gases have been prepared using it.

The operation of the system is as follows:

Preliminary

1. Assemble the system complete with sample containers. All glass joints should be clean and properly greased (Apiezon grease).

2. By-passing the diffusion pump, rough pump the system and check for any gross leaks by closing valve 1 and noting any increase in pressure on the manometer. Correct any leaks.

3. Immerse both traps in liquid nitrogen.

4. Switch on the diffusion pump and pump the system through the diffusion pump circuit.

5. The pressure should drop to less than 10^{-3} torr.

6. Close off the right arm (valve 2) of the manometer. The system is now ready for use.

Sample Preparation

The following directions are for the preparation of four standards containing the following compositions

Gas	Sample No.	1	2	3	4
X		0*	5	10	20
Y		100	95	90	80

* the concentrations are mol %

This is the procedure used for preparing the standards used in determining the limits of detection.

The basic technique is to fill each sample container with the gases, preferably in order of their increasing concentrations (pressures). Each gas is admitted at a pressure higher than that already in the container, back flow of gas from the sample container is therefore minimized. The total gas pressure used is approximately 500 torr.

The steps to be followed are:

1. If the gas X (and/or Y) is not in a storage container in the system it will have to be let into the system through the inlet valve. This is done by connecting the gas source to the inlet valve, the gas flow is turned on and should be at a pressure just above atmospheric. The manifold and the storage container is isolated from the pump and the sample containers. The gas is allowed in until a pressure of a few centimeters of mercury is noted on the manometer. It is then pumped out, bypassing the diffusion pump. This process is repeated three or four times before the sample container is filled to the required pressure.

2. Isolate the sample manifold from the pumping section by closing valve 1. Isolate all but the sample container of interest from the manifold.

3. Allow gas X to enter the manifold until the pressure is approximately that required (for no. 2 : 5 / 100 mole fraction x 500 torr = 25 torr). Record the exact pressure (P_i) from the manometer.

4. Isolate the sample container and then fill the others in a similar fashion. Then pump out gas X and prepare the system for gas Y (Step no. 1).

5. In adding the second gas its pressure should always be higher than the pressure in the sample container, until the required amount of gas has been added. This was conveniently done by using both sample container no. 1 (to contain Y only) and one of the 2 litre storage containers. Both were filled with Y to a pressure of approximately 650 torr (a more exact figure could be calculated using the volumes of the containers involved). The sample container of interest is then slowly opened until the pressure, as noted on the manometer, begins to fall at a fairly slow but steady rate. The sample container inlet valve should be just slightly open to achieve this. When the pressure has stopped falling (open the sample container valve a little more as a check), close the sample container valve. The pressure reading on the manometer is the total pressure (P_T) in the sample container.

6. Repeat for the other sample containers. Isolate container no. 1 and it will contain gas Y only.

7. Calculate the gas concentrations using:

$$\text{mol \%}_i = P_i \: / \: P_T \: X \: 100$$

8. Rotate each sample container to insure complete mixing before using.

Samples containing three gases were prepared using a slightly more complicated procedure. No check on the reproducibility of the method was done because of the poor reproducibility of the Auger electron spectrometer. However the nature of the analytical calibration curves indicated that the method was adequate for the present study.

5.7. Three Component Mixtures

A series of samples containing 5 mol % argon, 95 - 0 mol % N_2O, and 0 - 95 mol % acetylene were prepared. These samples were used to determine; the possible use of an internal standard, matrix absorption effect, and linear range of calibration curves.

The use of argon as an internal standard proved to be of little value. The calibration curves produced when plotting the net analyte signal / net argon signal were less linear than a plot of net analyte signal vs. concentration. This study did show that the signal intensity would vary greatly during the first ten minutes of analysis time, this effect was greatest for argon.

The linear range of the acetylene calibration curve extended over the entire 0 – 95 mol % range. The calibration curve for N_2O showed a positive deviation only at the 90 mol % level (Fig. 5.12). These curves indicated that absorption effects should be minimal. The maximum peak signal intensity was 15,000 counts per second.
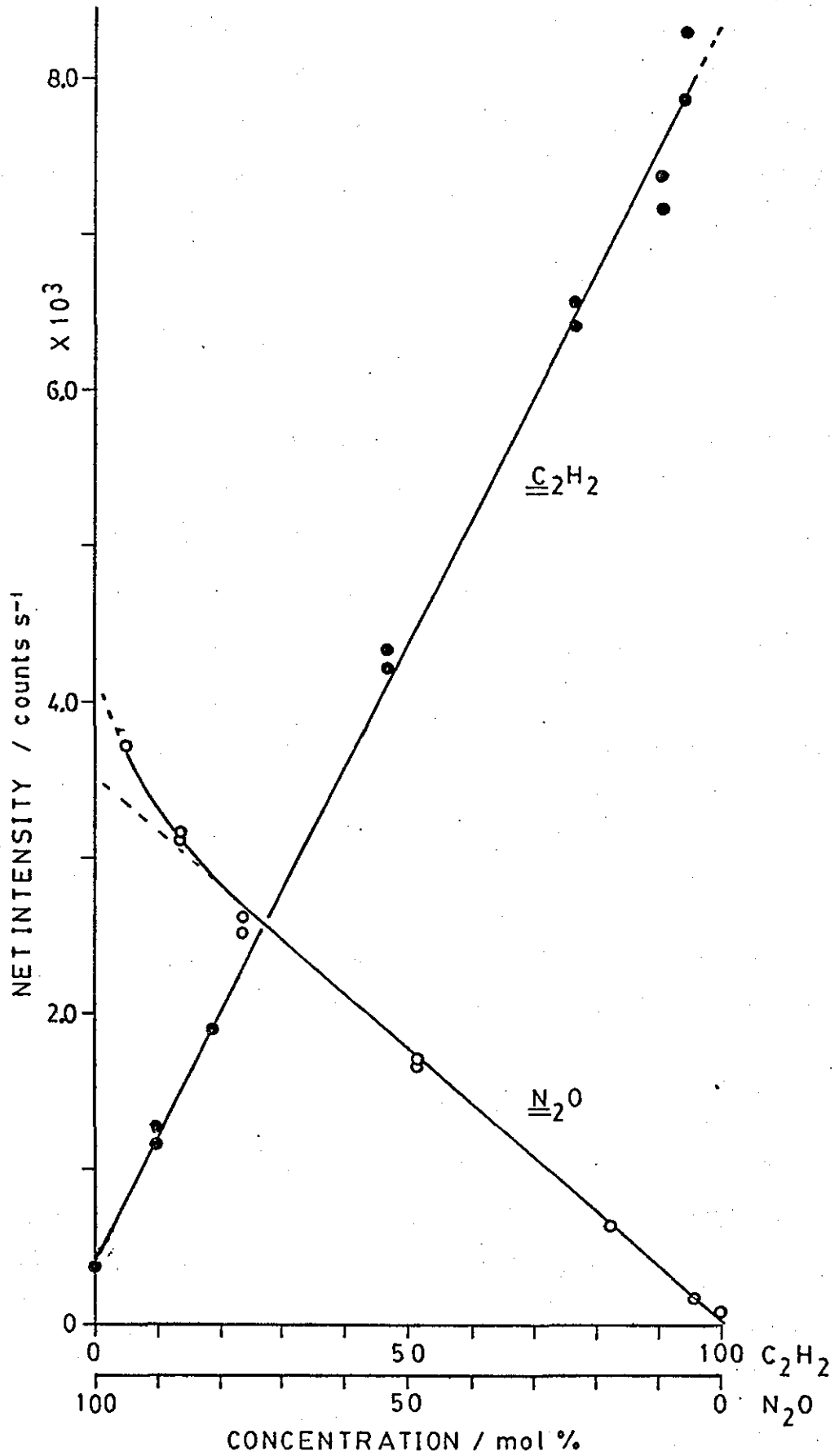
Fig. 5.12. The AES analytical calibration curves for the C of C_2H_2 and the N of N_2O.

Chapter 6

DISCUSSION

6.1. The AFM2 Spectrometer

The study of the spectrometer's operation has resulted in the
solution of many of the problems previously associated with it and
thus it has become a more reliable instrument.

Detailed studies of the operational parameters have helped in
selecting conditions resulting in better instrumental performance
for both qualitative and quantitative analysis. However, the per-
formance of the electron gun exciting source is unstable, probably
due to the reaction of the gun filament with the gases analyzed,
therefore exact predictions of parameter settings are not possible.
The results of the study should however assist in quickly redeter-
mining the best settings.

The addition of a scaler-timer unit to the output system was
easily accomplished and is necessary for quantitative analysis. It
would also be possible to feed the output pulse to an online com-
puter allowing data processing and more accurate spectra. However
other accessory equipment such as a stepping device for the analyzer
voltage would be necessary. Such additions would be expensive and
would require some basic design changes to the instrument. They
would be worthwhile if the study of spectral interpretation is to be
pursued. Spectra could then be stored for processing such as;
correction for spurious peaks, background subtraction, assigning
counting errors, and deconvolution of overlaping peaks.

A list of suggestions in regard to the spectrometer components
is as follows:

The Electron Gun

If the electron gun filament could be better isolated from the
analyte gases then its output would perhaps be more stable. Its
present instability limits quantitative analysis. This could perhaps
be accomplished by a redesign of the differential pumping system (Fig.
2.11), into which the gun is fitted, by the addition of a baffle plate
to make the gun less accessible to the analyte gas. An inert gas leak
into the filament chamber with or without the additional baffle might
also be effective. The present electron gun does not give the maxi-
mum beam current suggested by VG, and it is in need of repair. A
replacement would be advisable.

The Collision Chamber

The design of the collision chamber may be contributing to the high background intensity obtained; even without an analyte gas present (Fig. 4.1) a high background is obtained. Research into different chamber designs could perhaps result in a reduction of the background without adversely affecting the net Auger intensity. As the detection limit is $\propto (I_b)^{\frac{1}{2}}$ a large reduction would be necessary. Background intensity however may also be the result of electron scatter in the analyzer. Fioitzheim,[1] has reported a reduction (by a factor > 10) of spectral reflections of electrons from the deflection plates of a cylindrical analyzer by corrugating the plates.

Sample Introduction System

The pressure of gas in the spectrometer and the gun stack drops as the pressure in the gas expansion chamber drops; this necessitates an adjustment of the gas inlet valve. With the present system a spectrum cannot be recorded without a drop in sample pressure; the sample pressure is also difficult to reproduce. An automatic type of valve is required to maintain a constant gas pressure in the collision chamber.

Electron Detector

The channel electron multiplier has not been replaced during these studies although it was replaced once before during the previous studies. The multiplier is supposedly affected by sample gases, therefore its gain may be reduced. A new multiplier could be installed and its performance compared to the present one. The pulse distribution of the multiplier output could be analyzed on a multichannel analyzer to determine if the addition of a pulse height selector would be of advantage in reducing background (sec. 3.4.2). Probably an automatic means of shifting the "window" of a pulse selector would be required due to the variation of multiplier gain with electron signal intensity.

Analyzer

In surface analysis the energy distribution curve is not used in its simplest form because Auger peaks on the curve are small and are superimposed on a relatively high background. This is also the problem in detecting low concentrations (< 1 mol %) of gases. A possible solution may be to do the same as for surface analysis[2] i.e. to use the derivative (with respect to energy) of the energy distribution spectrum. Differentiation is accomplished electronically by applying a small a-c perturbation to the analyzer deflection plate potentials (or to the pedestal supply retardation potential) as they are swept

slowly across the energy range. The corresponding rapid fluctuations in the output of the detector are amplified and detected synchronously with a phase-sensitive detector that responds only to the applied fluctuations. (Refer to previous section on the collision chamber for an additional analyzer modification.)

6.2. Analytical Possibilities

Qualitative Analysis

The Auger spectra of the pure gases analyzed have been characteristic of the analyte; the presence of the elements in the gas molecule (hydrogen excepted) have also been determined. Gas mixtures however pose an analytical problem due to spectral overlap. If the gas mixture contains no gases having common elements then spectral overlap should be minimal and would be caused mostly by the overlap of the LMM spectra of the third row elements with each other or with the KLL spectra of the lower atomic number elements of the second row (Figs. 4.4, 4.5, 4.6). The spectral overlap of molecules containing common elements is a more difficult problem (Figs. 4.7, 4.12). As the spectra consist mostly of broad, rather than sharp, peaks, it is difficult to anticipate that the use of higher resolutions than those used in this study will result in much less spectral overlap. Also the decreased intensity resulting from increased resolution is a serious drawback and limits the resolution which can usefully be used. An example of this situation is detecting the presence of both CO and CO_2 in a mixture of the two (sec. 4.7.2); it can be done, however, very low concentrations of one in the presence of the other would probably be difficult to detect. Spectral deconvolution would be of assistance but the ability of the spectrometer to reproduce spectra would probably have to be improved.

Quantitative Analysis

This study has shown that it is possible to quantitatively determine the concentrations of gases in a simple mixture (up to three components were used) where no spectral overlap occurs. The calibration curves obtained were linear over wide concentration ranges (Figs. 5.5 - 5.10); negative deviations where they occured are attibuted to counting losses. Matrix absorption affects were not observed. The high background intensities limit the detection limits obtainable (Tables 5.4, 5.5); they range from 0.01 (Ar) to 0.40 (O in CO) mol %. The normal concentrations[3] of trace gases in atmospheric air is much lower than these limits. Therefore the use of AES in its present state, is not generally applicable to air pollution analysis.

Comparison with other Instrumental Methods of Gas Analysis

It is difficult to compare AES to other instrumental methods of gas analysis as it is a new technique in an early stage of development, and others such as mass spectrometry, gas-chromatography, and I.R. spectrometry to which it could be compared, are established and highly refined instrumental techniques. Another difficulty is the various capabilities of the established instruments, which range from simple to highly sophisticated designs. Even in cost, a comparison is difficult as AES does not have the advantages of mass production.

The applications of AES (in the gas phase) can be categorized into two groups, those in which the technique is used as a tool for analysis and those in which the spectra are studied for the insight they give into molecular electronic structure. It is the former application which is considered here.

AES has a number of characteristics that make it suitable as a tool for qualitative and quantitative analysis. These include the ability to:
- determine all elements (except H and He), but particularly the light elements.
- identify pure compounds from their spectra.
- simultaneously determine two or more forms of the same element which differ in chemical environment.
- determine several gases in a mixture.

In regards to quantitative analysis of gases the Auger band (peak) intensities are proportional to the partial pressure of components in a mixture. A special feature of the technique is the small amount and the low pressure of the gas required for analysis. Although the gas pressure in the collision chamber of the present instrument cannot be measured it is probably about 0.1 torr. Since gas components at a concentration as low as 0.01 mol % can be measured, therefore the partial pressure of components may be as low as 10^{-5} torr (for Ar). However, AES also has a number of unfavourable characteristics which include spectral overlap, high background intensities, and limited detection limits.

Virden[4] has discussed the various instrumentation available for gas analysis. Mass spectrometry is used for N_2, O, CO, CO_2, and to a lesser degree for H_2O and CH_4 analysis. It is considerably more expensive and complex than gas chromatography and I.R. spectrometry, . and in these aspects AES will probably be similar. The advantages of mass spectrometry are precision, speed of response, and capability of

measuring all gases; its sensitivity is down to 0.05 ppm (5×10^{-13} torr of argon is detectable). I.R. spectrometry is used for CO, CO_2, and to a lesser degree for CH_4, C_2H_4, H_2O, N_2O, NO, NH_3, SO_2, and other organics. Simple nonpolar diatomics such as O_2, N_2, H_2 and Cl_2 cannot be determined by I.R. but all other common gases can be. The method is not as versatile or selective as gas chromatography but it is simple and direct reading. Most I.R. analyzers are used to monitor CO and CO_2. Some minimum detection limits claimed for a commercial I.R. gas analyzer (MIRAN ® IA) are as follows: NH_3 – 0.2 ppm, N_2O – 0.07 ppm, CO – 0.20 ppm, CO_2 – 0.05 ppm and SO_2 – 0.5 ppm. Gas chromatography can be used for virtually any organic compound and all gases. It is the most versatile and selective of the methods available for gas analysis. Detection limits of 5 ppb have been reported[5] for SO_2 and H_2S in air.

The combination of gas chromatography and mass spectrometry has proved a powerful analytical tool despite the problems associated with the interfacing of the two instruments which operate at vastly different pressures. Such a combination has been made between a gas chromatograph and a photoelectron spectrometer.[6] The interfacing devices which have been developed should be directly applicable to the coupling of a gas chromatograph to the Auger spectrometer and it is envisaged that such a combination would add a new dimension to the analytical possibilities of gas phase Auger electron spectrometry.

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APPENDIX A. System Component Instruction Manuals

Component	Title	Number
ED330		
ED50	Edwards high speed rotary pumps	M03894 / 5
V11	Edwards high vacuum solenoid valve	M08635 / 1,3,4
VSK1	Edwards operating instructions	M07612 / 3
PVG-1	Vacuum generators operating instructions	01.463
EO4	Edwards oil vapour diffusion pumps	M05606 / 6
EO2	Edwards oil vapour diffusion pumps	M05638 / 6
CCT100		
CCT50	Vacuum generators UHV cold traps	06001376
V1G20 (1)		
V1G20 (2)	Vacuum generators technical information bulletin	01.454
V5		
V16	Vacuum generators technical information bulletin	01.302
V20		
V21		
System Control	Eurotherm temperature controller model LP48-HS-R2, Eurotherm application note	AN101

PRINCIPAL AUGER ELECTRON ENERGIES

Dots indicate the electron energies of the principal Auger peaks for each element. Large dots represent predominant peaks for each element. All data was recorded under similar conditions using the same Auger Electron Spectroscopy System.

MNN

LMM

KLL

ATOMIC NUMBER

ELECTRON ENERGY (eV)

PHYSICAL ELECTRONICS INDUSTRIES, INC.
7317 SOUTH WASHINGTON AVENUE • EDINA, MINNESOTA 55435
Telephone (812) 941-5540   Telex 29-0107

Printed in U.S.A.

APPENDIX C. Auger Spectra

Compound	Element	Energy Range eV	Analyzer settings eV / mm
O_2	O	450 — 550	50 / 2
		485 — 515	50 / 2
C_2H_2	C	200 — 300	50 / 2
		240 — 270	50 / 2
CO	C	200 — 300	50 / 2
		200 — 300	20 / 2
		240 — 270	50 / 2
		240 — 270	20 / 2
	O	450 — 550	50 / 2
		480 — 510	50 / 2
CO_2	C	200 — 300	50 / 2
		240 — 270	50 / 2
	O	450 — 550	50 / 2
		480 — 510	50 / 2
N_2	N	300 — 400	50 / 2
		355 — 385	50 / 2
NH_3	N	300 — 400	50 / 2
		355 — 385	50 / 2
N_2O	N	300 — 400	50 / 2
		355 — 385	50 / 2
	O	450 — 550	50 / 2
		485 — 515	50 / 2
NO	N	300 — 400	50 / 2
		300 — 400	20 / 2
		355 — 385	50 / 2 [1]
		355 — 385	50 / 2 [2]
	O	450 — 550	50 / 2
		480 — 510	50 / 2
NO_2	N	300 — 400	50 / 2
		355 — 385	50 / 2
	O	450 — 550	50 / 2
		485 — 515	50 / 2

Compound	Element	Energy Range eV	Analyzer settings eV / mm
Ne	Ne	730 — 830	50 / 2
		730 — 830	20 / 2
H_2S	S	105 — 205	50 / 2
		105 — 205	20 / 2
		120 — 150	50 / 2
		120 — 150	20 / 2
SO_2	S	105 — 205	50 / 2
		125 — 155	50 / 2
CCl_4	Cl	125 — 225	20 / 2
		155 — 185	20 / 2
Ar	Ar	140 — 240	20 / 2
		180 — 210	20 / 2

1.   Maximum Beam Current 150 μA

2.   Maximum Beam Current 500 μA

O AUGER
OF O$_2$

Date 3/4/78
Spectrum No. 9
Sample O$_2$ ~90%
Ar ~10%
sam 17.5 t
Press ana 1.2×10^{-5}
gun 2×10^7

ENERGY SOURCE
Fil curr 2.8 A
Gun curr 1 µA
Voltage 5 kV
X 345 Y 640 F 5.38
Max gun curr 315 µA
ANALYZER
Energy 50 V
Slits 2 mm

SCAN
Pedestal 450 V
Amplitude 100 V
Time 300 s
Counts 1×10^4 s^{-1}
T.C. 0.33 s
Zero supp —
Exp x —

DETECTOR
Mult 3.2 kV
E Set 100
Mag trim mA

O AUGER
OF O$_2$

Date 3/4/78
Spectrum No. 10
Sample O$_2$ ~90%
Ar ~10%
sam 17 t
Press ana t
gun 2×10^7

ENERGY SOURCE
Fil curr 2.8 A
Gun curr 1 µA
Voltage 5.0 kV
X 345 Y 6.4 F 5.38
Max gun curr 510·280 µA
ANALYZER
Energy 50 V
Slits 2 mm

SCAN
Pedestal 485 V
Amplitude 30 V
Time 300 s
Counts 1×10^4 s^{-1}
T.C. 0.33 s
Zero supp —
Exp x —

DETECTOR
Mult 3.2 kV
E Set 100
Mag trim — mA

C AUGER OF C₂H₂

C AUGER OF C₂H₂

CARBON
K LL AUGER
OF
CARBON MONOXIDE

Argon

INTENSITY/counts s^{-1}

$\times 10^4$

ELECTRON KINETIC ENERGY/eV

Date 29/3/78
Spectrum No. 10
Sample CO ~95 %
Ar ~5 %

sam 17 t
Press ana 1.5×10^{-5} t
gun 2×10^{-7} t

ENERGY SOURCE
Fil curr 2.6 A
Gun curr 1 µA
Voltage 5 kV
X 3.58 Y 6.45 F 5.45
Max Gun curr 360 µA

ANALYZER
Energy 50 V
Slits 2 mm

SCAN
Pedestal 200 V
Amplitude 100 V
Time 300 s
Counts 3×10^4 s^{-1}
T.C. .33 s
Zero supp −
Exp x −

DETECTOR
Mult 3.2 kV
E Set 50
Mag trim / mA

C AUGER
OF CO

INTENSITY/counts s^{-1}

$\times 10^4$

ELECTRON KINETIC ENERGY/eV
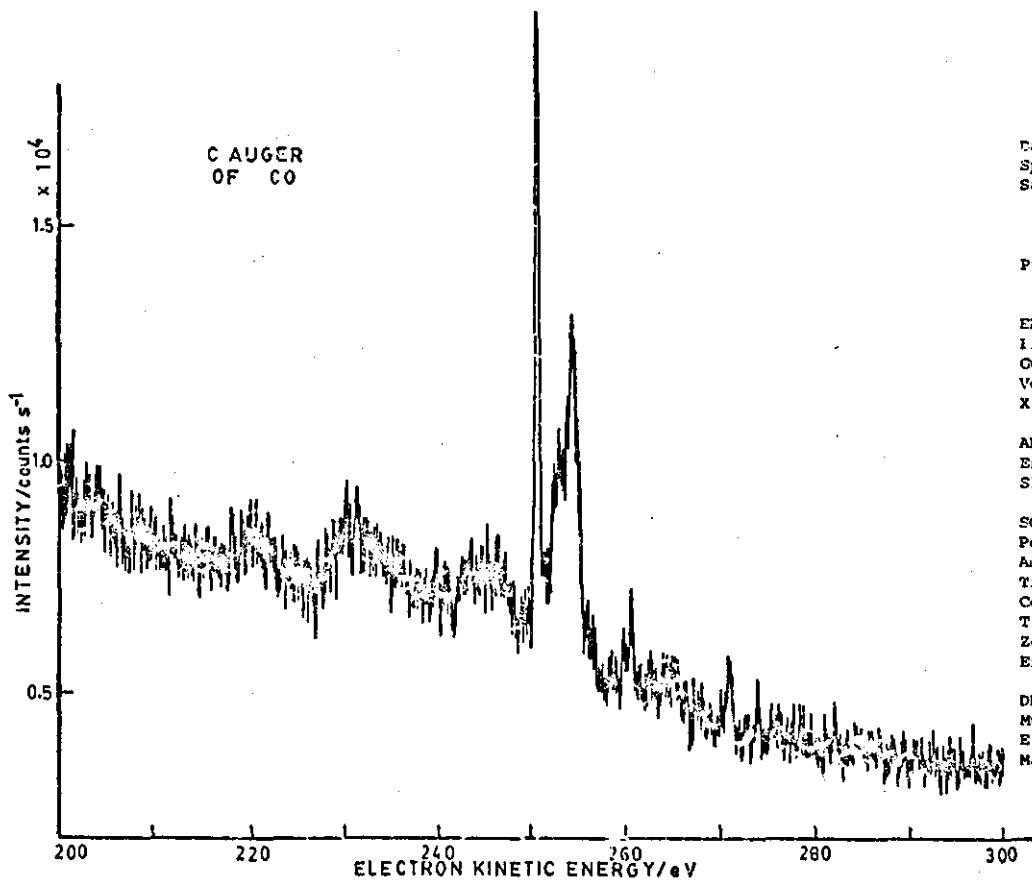
Date 16/5/78
Spectrum No. 5
Sample CO

sam 10 t
Press ana t
gun 2×10^{-7} t

ENERGY SOURCE
Fil curr 3.4 A
Gun curr ~200 µA
Voltage 5 kV
X Y F
Max Gun curr 189 µA

ANALYZER
Energy 20 V
Slits 2 mm

SCAN
Pedestal 200 V
Amplitude 100 V
Time 300 s
Counts 1×10^3 s^{-1}
T.C. 0.33 s
Zero supp 0.19
Exp x 1

DETECTOR
Mult 3.2 kV
E Set 100
Mag trim mA

C AUGER
OF CO

Date 29/3/78
Spectrum No. 9
Sample
CO ₋95 %
Ar ₋ 5 %
sam 10 t
Press ana 1.5 x 10⁻⁶ t
gun 2 x 10⁻⁷ t

ENERGY SOURCE
Fil curr 2.6 A
Gun curr 1 µA
Voltage 6 kV
X 3.38 Y 6.40 F 5.45
Max gun curr 360µA
ANALYZER
Energy 50 V
Slits 2 mm

SCAN
Pedestal 240 V
Amplitude 30 V
Time 300 s
Counts 3 x 10⁴ s⁻¹
T.C. 0.33 s
Zero supp -
Exp x ·

DETECTOR
Mult 3.2 kV
E Set 50/1000
Mag trim - mA

C AUGER
OF CO

Date 18/5/78
Spectrum No. 4
Sample
CO
sam 10 t
Press ana t
gun 2 x 10⁻⁷ t

ENERGY SOURCE
Fil curr 3.4 A
Gun curr ~200 µA
Voltage 5 kV
X Y F
Max Gun curr 180µA
ANALYZER
Energy 20 V
Slits 2 mm

SCAN
Pedestal 240 V
Amplitude 30 V
Time 300 s
Counts 3 x 10³ s⁻¹
T.C. 0.33 s
Zero supp -
Exp x -

DETECTOR
Mult 3.2 kV
E Set 100
Mag trim mA

O AUGER
OF CO

Date 29/3/78
Spectrum No. 10
Sample
CO ~95%
Ar ~5%
sam 70   t
Press ana 1.5 x10⁵ t
gun 2 x10⁷ t

ENERGY SOURCE
Fil curr 2.6   A
Gun curr 1   μA
Voltage 5   kV
X 3.38 Y 6.40 F 5.45
Max gun curr 360μA
ANALYZER
Energy 50   V
Slits 2   mm

SCAN
Pedestal 450   V
Amplitude 100   V
Time 300   s
Counts 3 x10³   s⁻¹
T.C. 0.33   s
Zero supp 0.5
Exp x   1

DETECTOR
Mult 3.2   kV
E Set 50/1000
Mag trim —   mA

O AUGER
OF CO
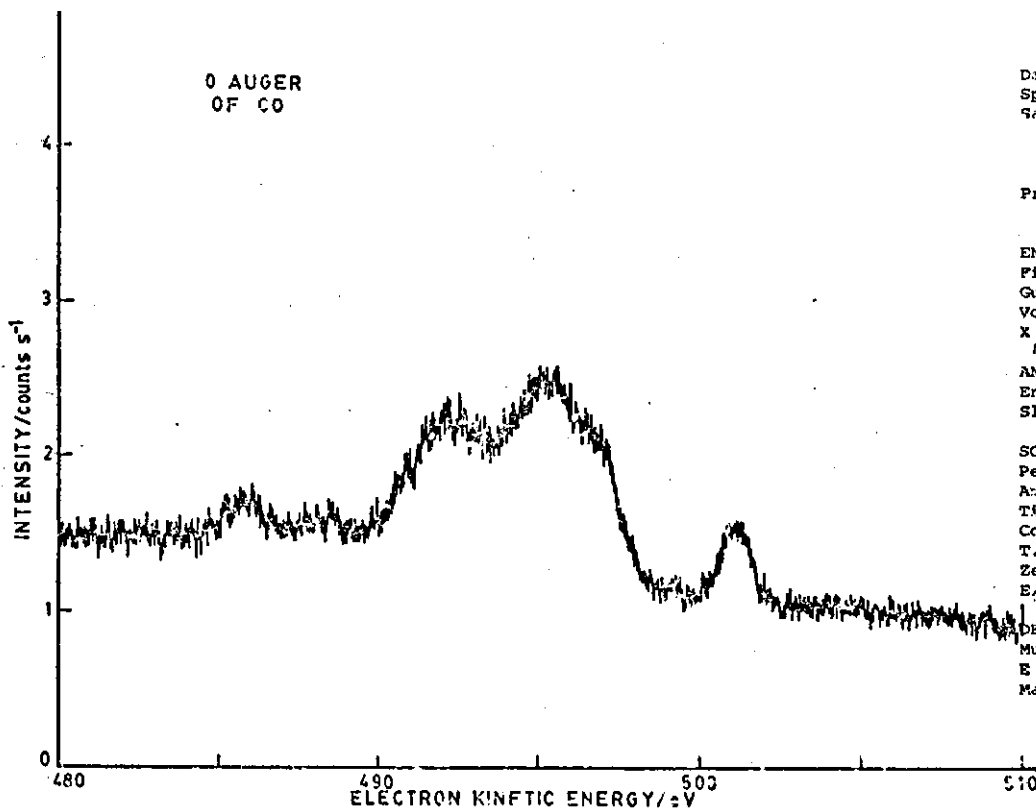
Date 18/5/78
Spectrum No. 7
Sample
CO

sam 10   t
Press ana   t
gun 2 x10⁷ t

ENERGY SOURCE
Fil curr   A
Gun curr   μA
Voltage   kV
X Y F
Max gun curr 189μA
ANALYZER
Energy 50   V
Slits 2   mm

SCAN
Pedestal 480   V
Amplitude 30   V
Time 300   s
Counts 3 x10²   s⁻¹
T.C. 0.33   s
Zero supp —
Exp x —

DETECTOR
Mult 3.2   kV
E Set 100
Mag trim —   mA

CARBON KLL AUGER OF CARBON DIOXIDE

C AUGER OF CO_2

O AUGER OF CO_2

Date 30/5/78
Spectrum No. 6
Sample CO_2 ~95%
Ar ~ 5%
sam 17 t
Press ana 1.5×10⁻⁵ t
gun 2×10⁻⁷ t

ENERGY SOURCE
Fil curr 2.8 A
Gun curr 1 µA
Voltage 5 kV
X 3.38 Y 6.41 F 5.45
Max gun Curr 850µA

ANALYZER
Energy 50 V
Slits 2 mm

SCAN
Pedestal 450 V
Amplitude 100 V
Time 300 s
Counts 1×10⁴ s⁻¹
T.C. 0.33 3×10⁸ s
Zero supp — 1 .7
Exp x — 1 ×1

DETECTOR
Mult 3.2 kV
E Set 50/1000
Mag trim — mA

O AUGER OF CO_2

Date 16/5/78
Spectrum No. 6
Sample CO_2
sam 17 t
Press ana t
gun 2×10⁻⁷ t

ENERGY SOURCE
Fil curr 3.4 A
Gun curr ~ 200 µA
Voltage 5 kV
X Y F

ANALYZER
Energy 50 V
Slits 2 mm

SCAN
Pedestal 480 V
Amplitude 30 V
Time 300 s
Counts 3×10³ s⁻¹
T.C. 0.33 s
Zero supp —
Exp x —

DETECTOR
Mult 3.2 kV
E Set 100
Mag trim — mA

N
KLL AUGER
OF N₂

INTENSITY/counts s⁻¹

$\times 10^4$

15

10

0.5

0

ELECTRON KINETIC ENERGY/eV

300 320 340 360 380 400

Date 29/3/78
Spectrum No. 6
Sample
    N₂ ~95%
    Ar ~5%
    sam 15   t
Press ana 9×10⁻⁶ t
    gun 1.5×10⁻⁷ t

ENERGY SOURCE
Fil curr 2.6   A
Gun curr 1   µA
Voltage 5   kV
X 3.38 Y 6.40 F 5.45
Max gun curr 350µA
ANALYZER
Energy 50   V
Slits 2   mm

SCAN
Pedestal 300   V
Amplitude 100   V
Time 300   s
Counts 1×10⁴ s⁻¹
T.C. 0.33   s
Zero supp —
Exp x —

DETECTOR
Mult 3.2   kV
E Set 100
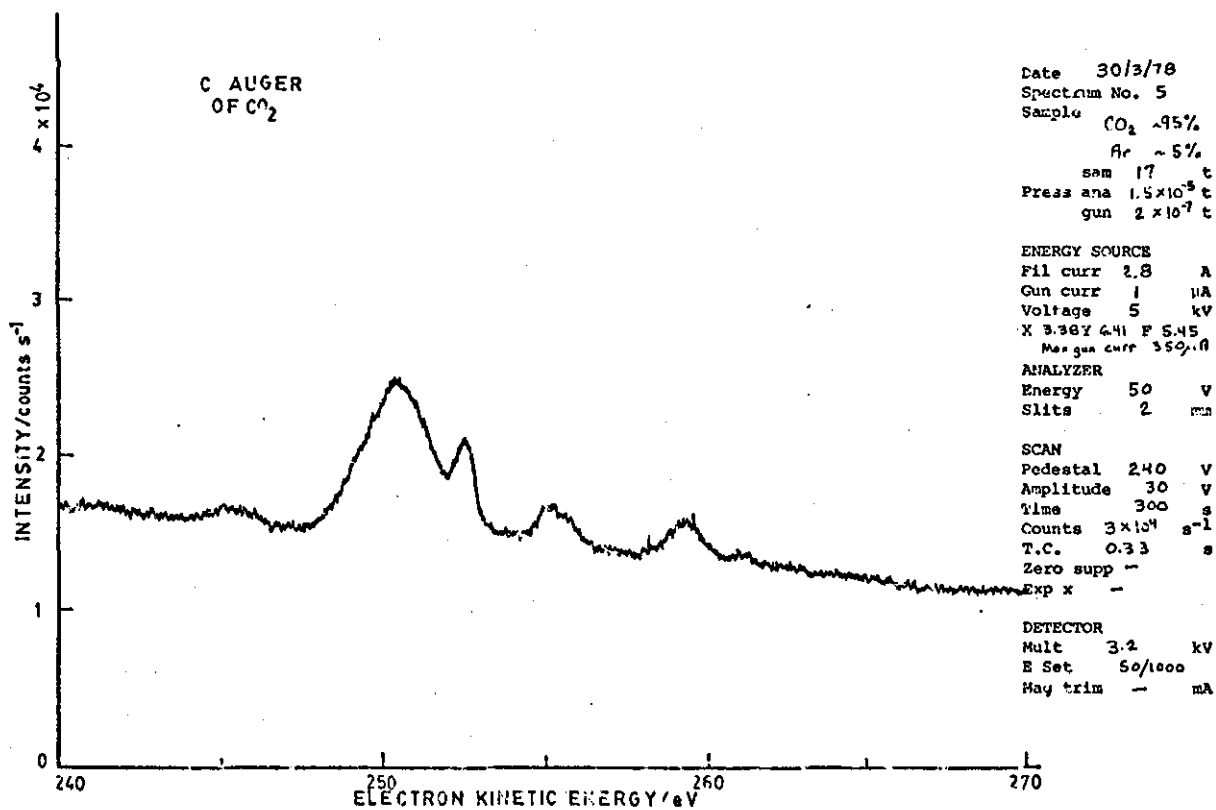Mag trim —   mA

KLL AUGER
OF
NITROGEN

INTENSITY/counts s⁻¹

$\times 10^4$

15

10

0.5

0

ELECTRON KINETIC ENERGY/eV

355 365 375 385

Date 29/3/78
Spectrum no. 5
Sample
    N₂ ~95%
    Ar ~5%
    sam 15   t
Press ana 7.×10⁻⁶ t
    gun 1×10⁻⁷ t

ENERGY SOURCE
Fil curr 2.6   A
Gun curr 1   µA
Voltage 5   kV
X 343 Y 640 F 5.68
Max gun curr 350µA
ANALYZER
Energy 50   V
Slits 2   mm

SCAN
Pedestal 355   V
Amplitude 30   V
Time 300   s
Counts 1×10⁴ s⁻¹
T.C. .33   s
Zero supp —
Exp x —

DETECTOR
Mult 3.2   kV
E Set 100
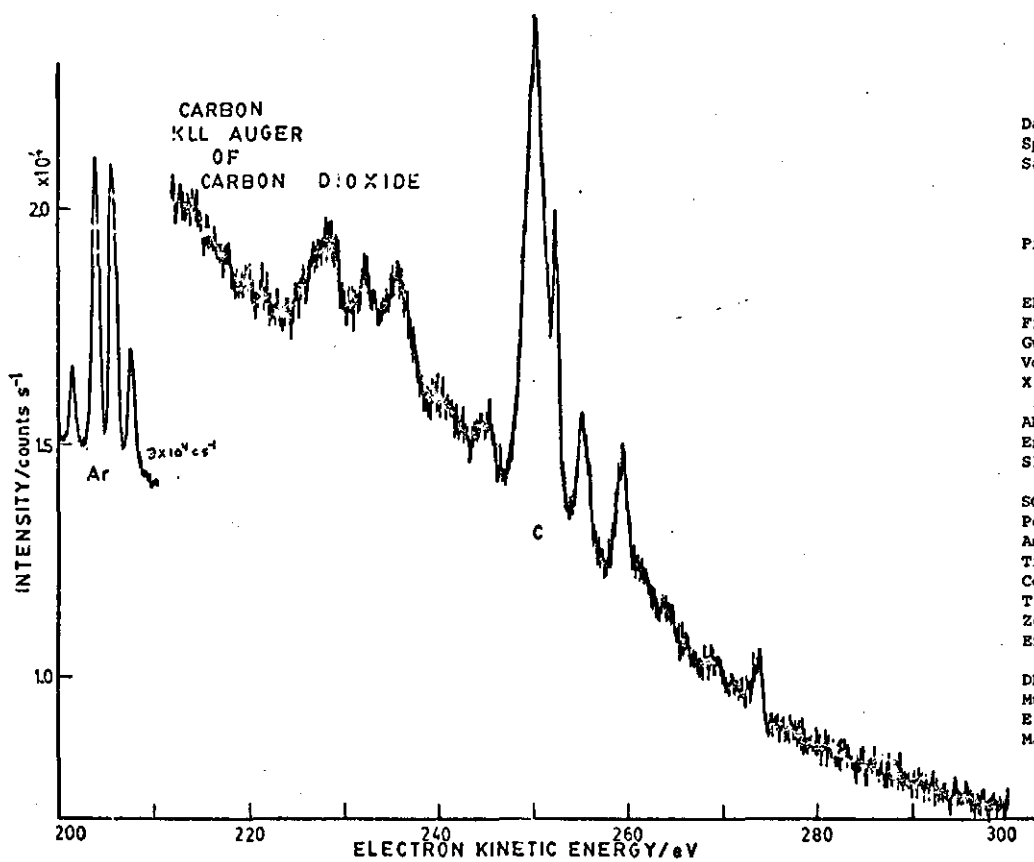Mag trim —   mA

N AUGER
OF NH₃

Date 31/3/78
Spectrum No. 11
Sample
    NH₃ ~95 %
    Ar ~5 %
    sam 16 t
Press ana 1.5×10⁻⁵ t
    gun 2 ×10⁻⁷ t

ENERGY SOURCE
Fil curr 2.6 A
Gun curr 1 μA
Voltage 5 kV
X 3.37 Y 6.11 F 5.55
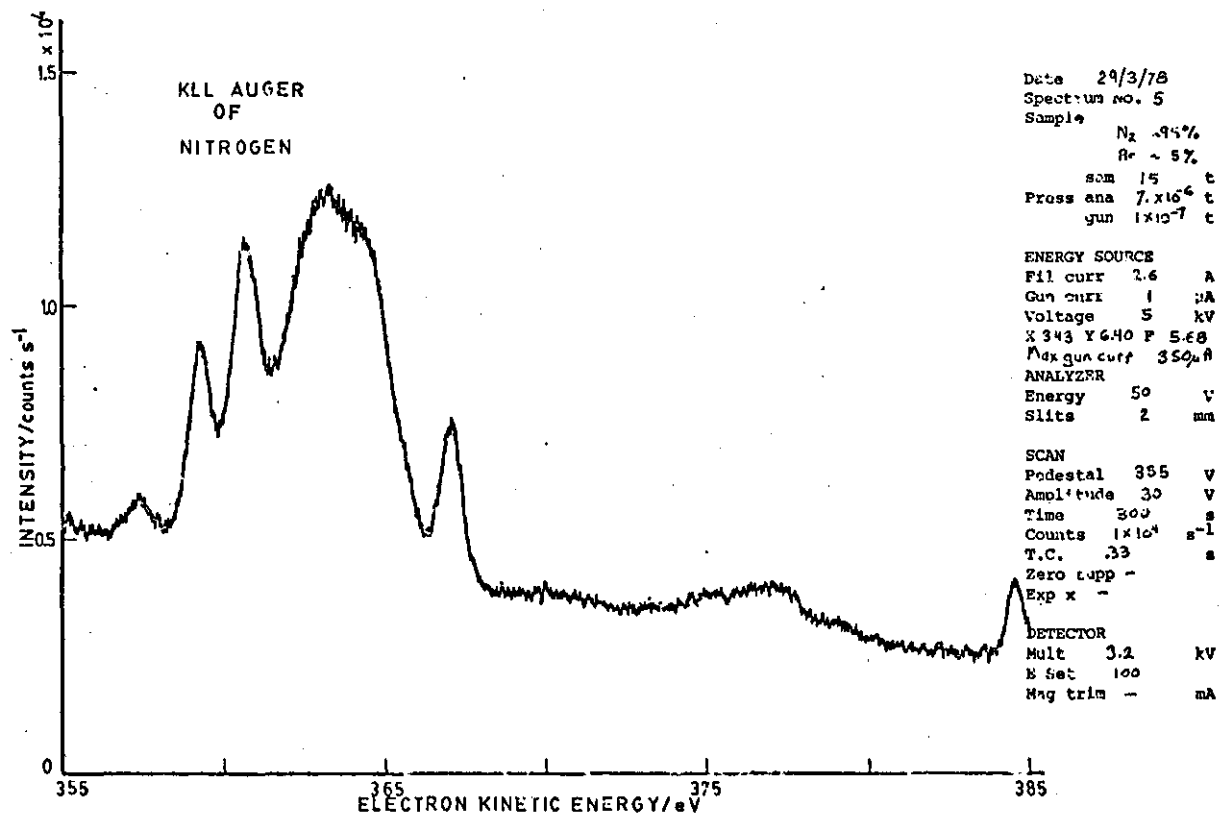
ANALYZER
Energy 50 V
Slits 2 mm

SCAN
Pedestal 300 V
Amplitude 100 V
Time 300 s
Counts 1×10¹ s⁻¹
T.C. 0.33 s
Zero supp 0.3
Exp x 3

DETECTOR
Mult 3.2 kV
E Set 100/1000
Mag trim — mA

Zero supp
= 0.0

N AUGER
OF NH₃

Date 31/3/78
Spectrum No. 14
Sample
    NH₃ ~95 %
    Ar ~5 %
    sam 14.5 t
Press ana 1.5×10⁻⁵ t
    gun 2×10⁻⁷ t

ENERGY SOURCE
Fil curr 2.6 A
Gun curr 1 μA
Voltage 5 kV
X 3.37 Y 6.11 F 5.55
Max gun curr 375μA
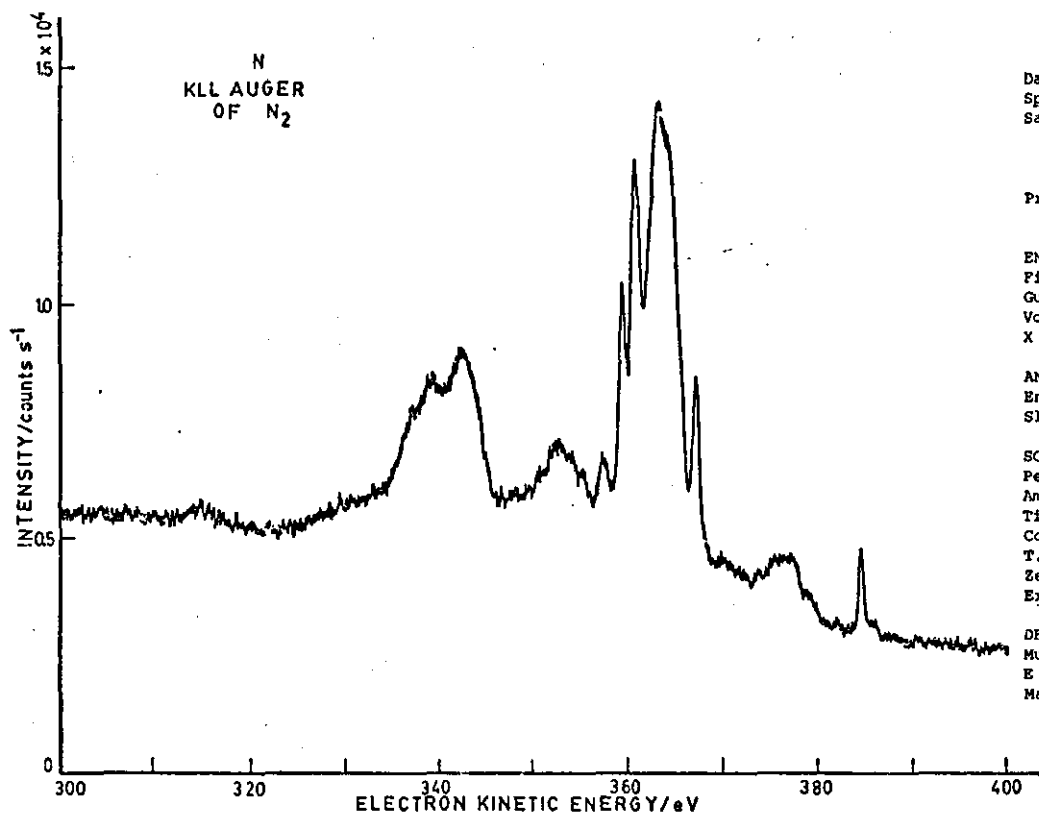ANALYZER
Energy 50 V
Slits 2 mm

SCAN
Pedestal 365 V
Amplitude 30 V
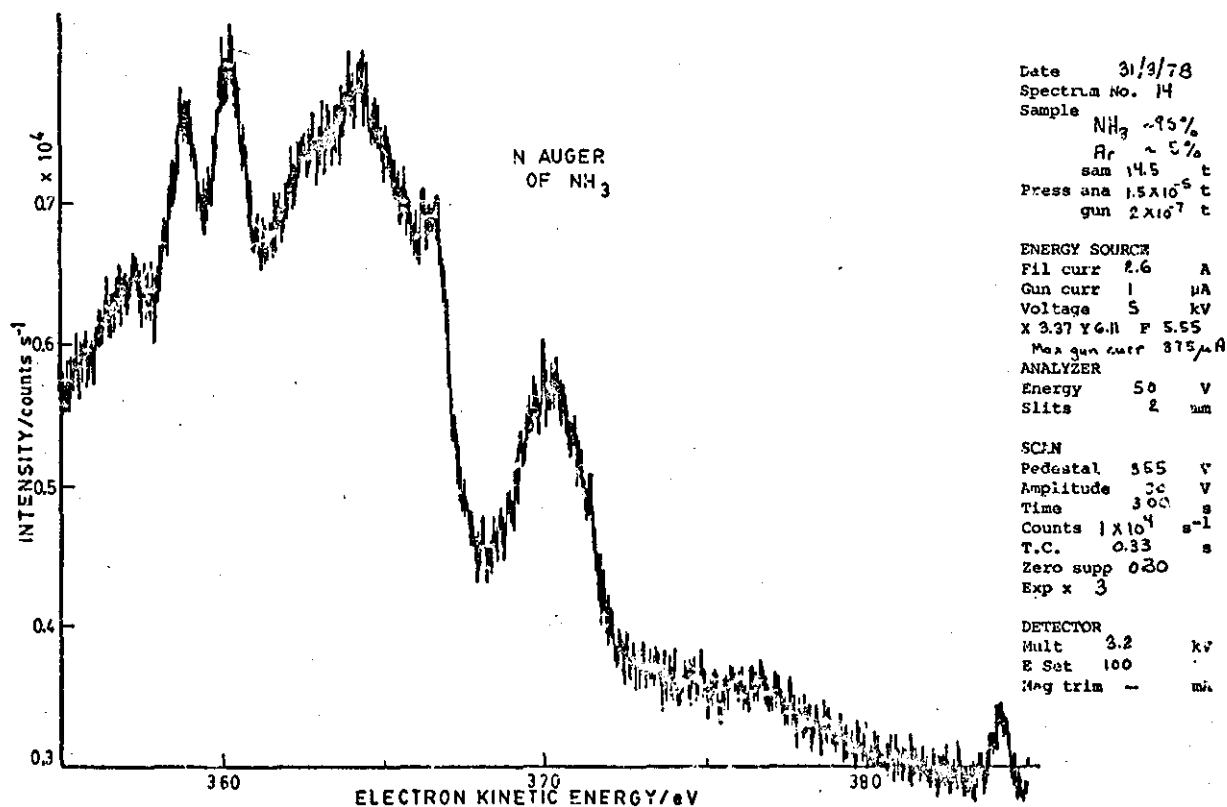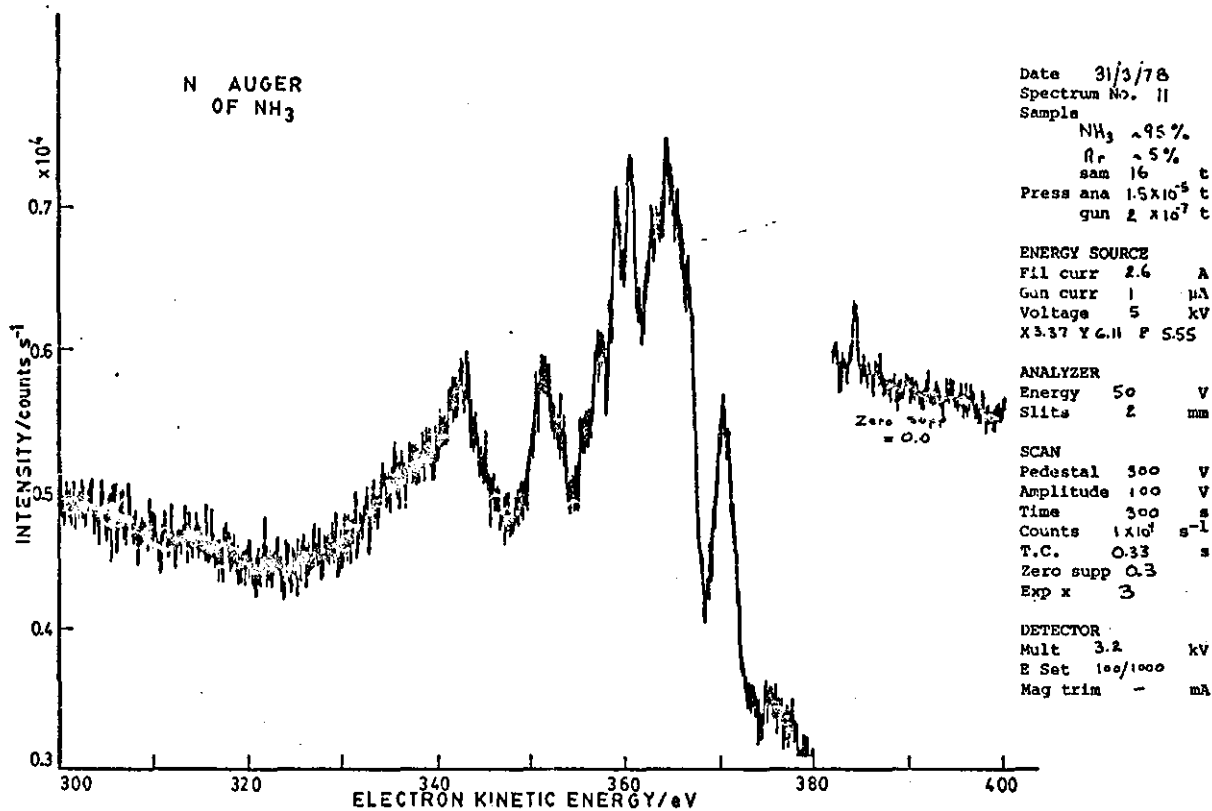Time 300 s
Counts 1×10⁴ s⁻¹
T.C. 0.33 s
Zero supp 030
Exp x 3

DETECTOR
Mult 3.2 kV
E Set 100
Mag trim — mA

N AUGER
OF N₂O

N AUGER
OF N₂O

O AUGER OF N_2O

O AUGER OF N_2O

N AUGER
OF NO

Date 26/6/78
Spectrum No. 5
Sample NO

sam 15 t
Press ana t
gun 2 X 10⁻⁷ t

ENERGY SOURCE
Fil curr 3.0 A
Gun curr 200 µA
Voltage 5 kV
X 5.51 Y 3.32 F 10
Maxgun curr 500µA
ANALYZER
Energy 50 V
Slits 2 mm

SCAN
Pedestal 300 V
Amplitude 100 V
Time 300 s
Counts 1X10⁴ s⁻¹
T.C. 0.33 s
Zero supp 0.4
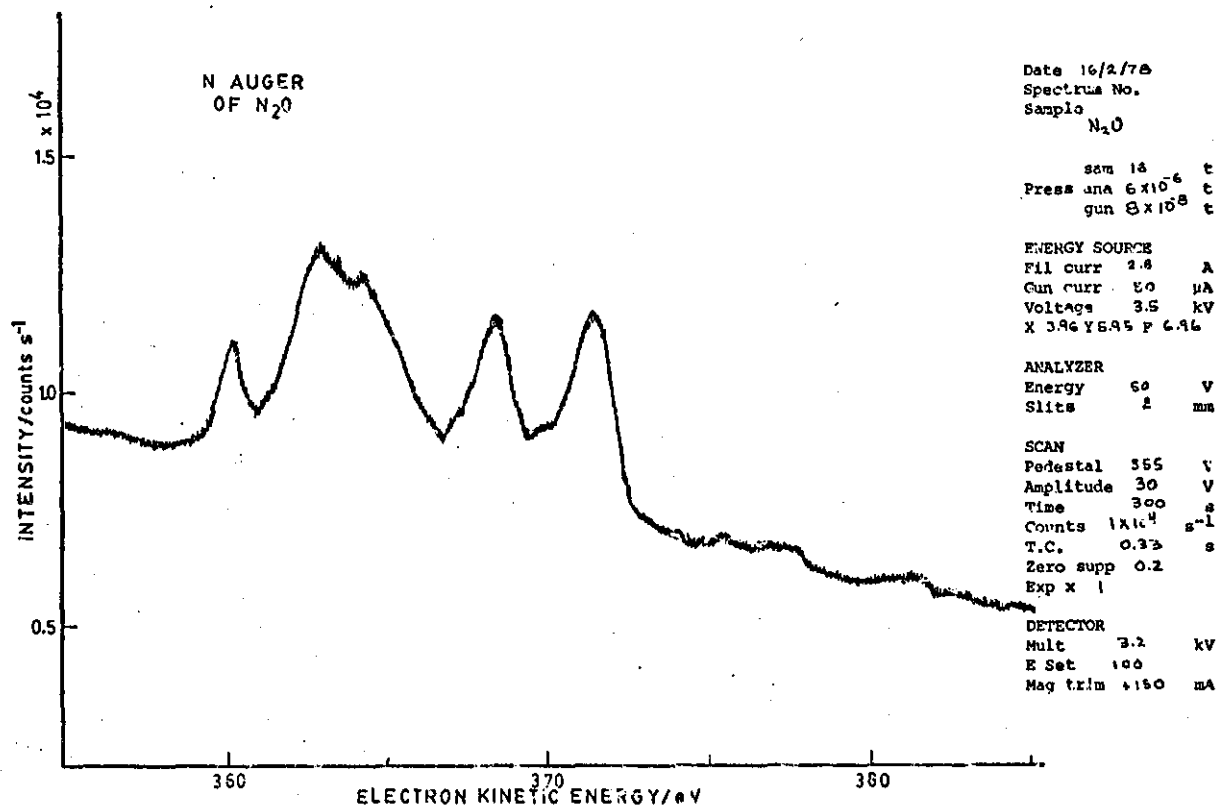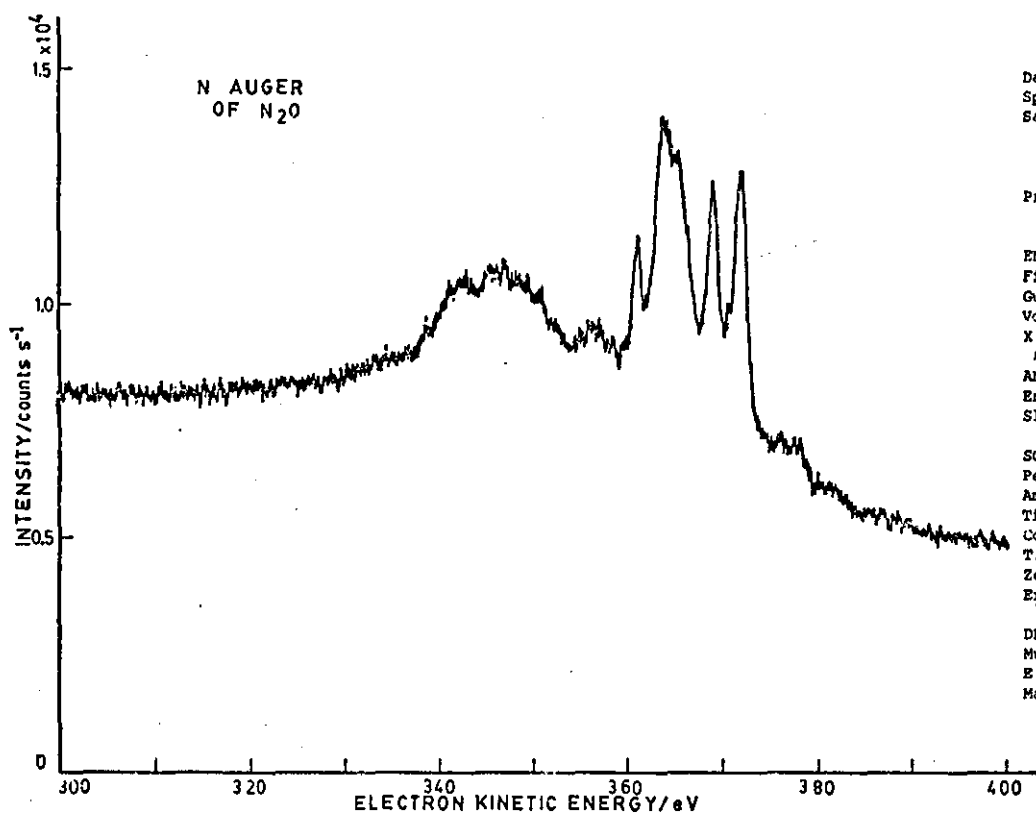Exp x 1

DETECTOR
Mult 3.2 kV
E Set 100/1000
Mag trim — mA

N AUGER
OF NO

Date 26/6/78
Spectrum No. 6
Sample NO

sam 15 t
Press ana t
gun 2x10⁻⁷ t

ENERGY SOURCE
Fil curr 3 A
Gun curr 200 µA
Voltage 5 kV
X 5.51 Y 3.32 F 10
Maxgun curr 500µA
ANALYZER
Energy 20 V
Slits 2 mm

SCAN
Pedestal 300 V
Amplitude 100 V
Time 300 s
Counts 1X10³ s⁻¹
T.C. 0.33 s
Zero supp 0.8
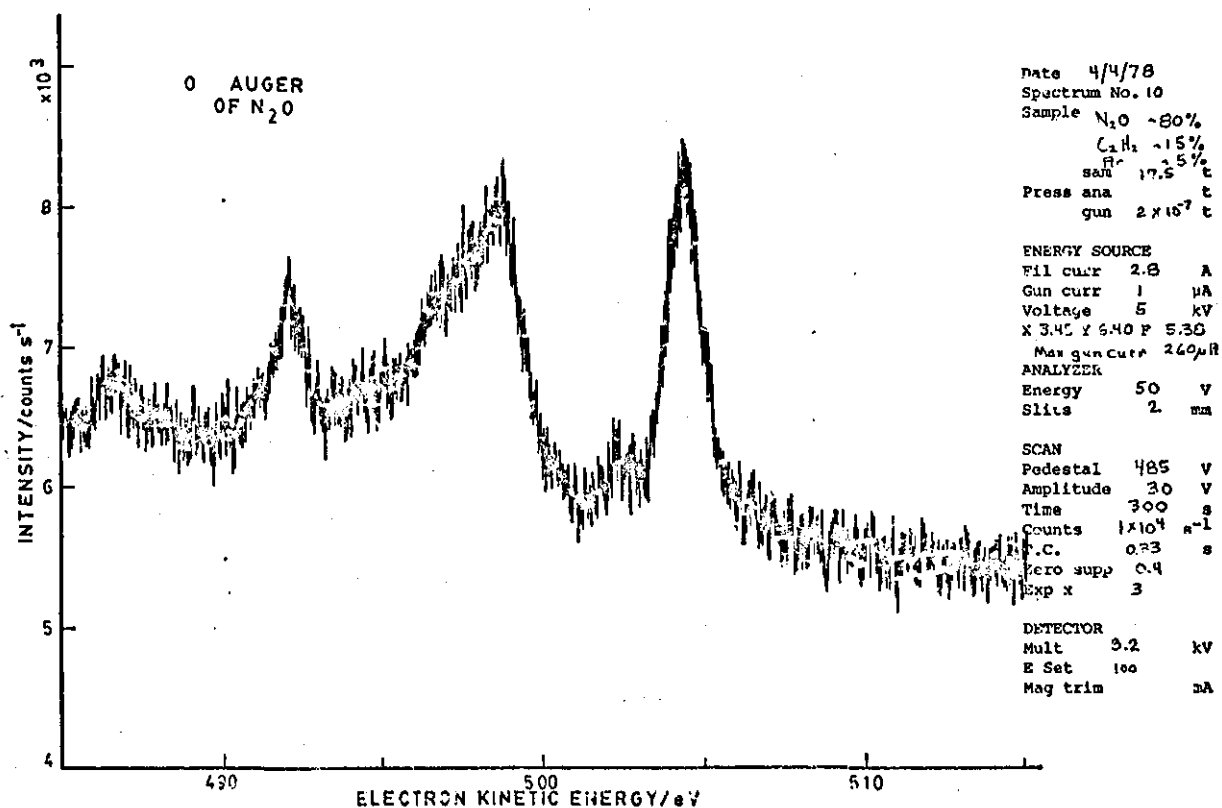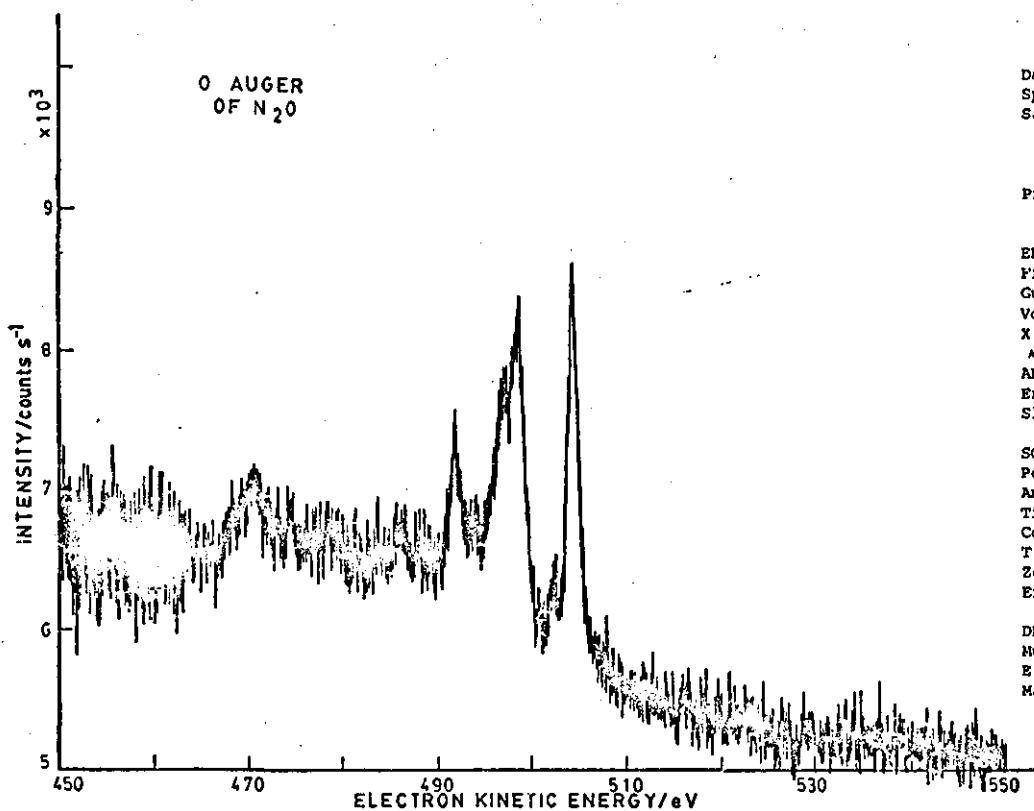Exp x 1.0

DETECTOR
Mult 3.2 kV
E Set 100/1000
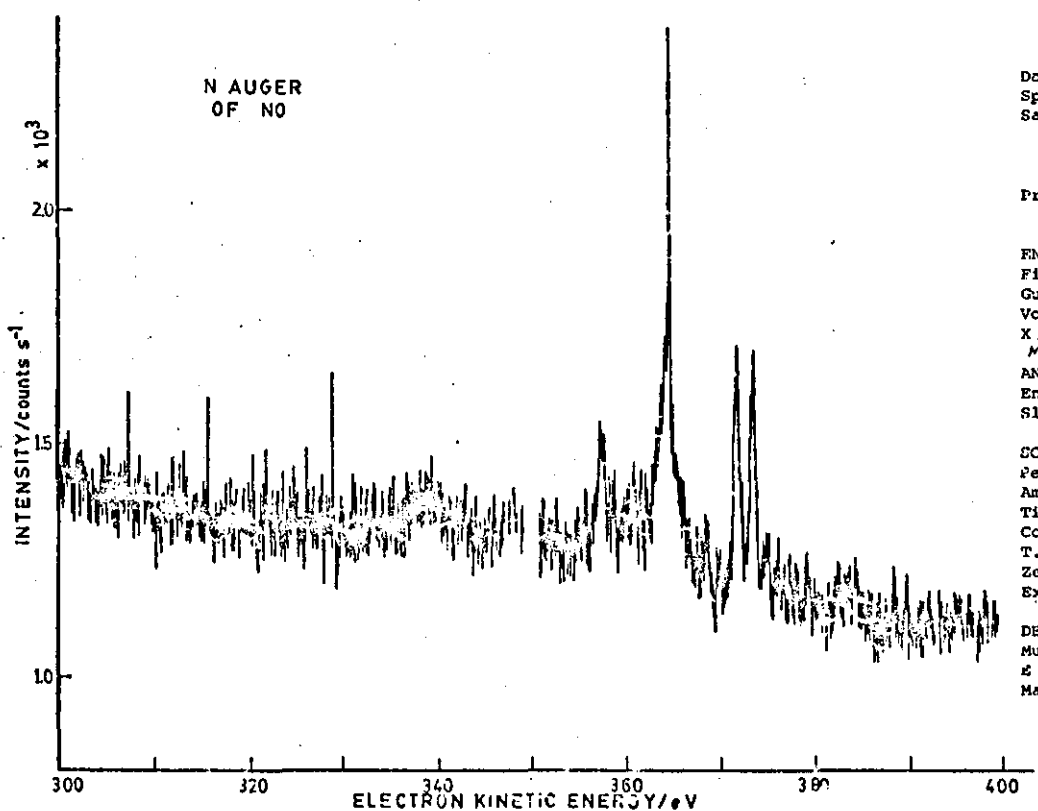Mag trim mA

N AUGER
OF NO

INTENSITY/counts s⁻¹ — × 10³

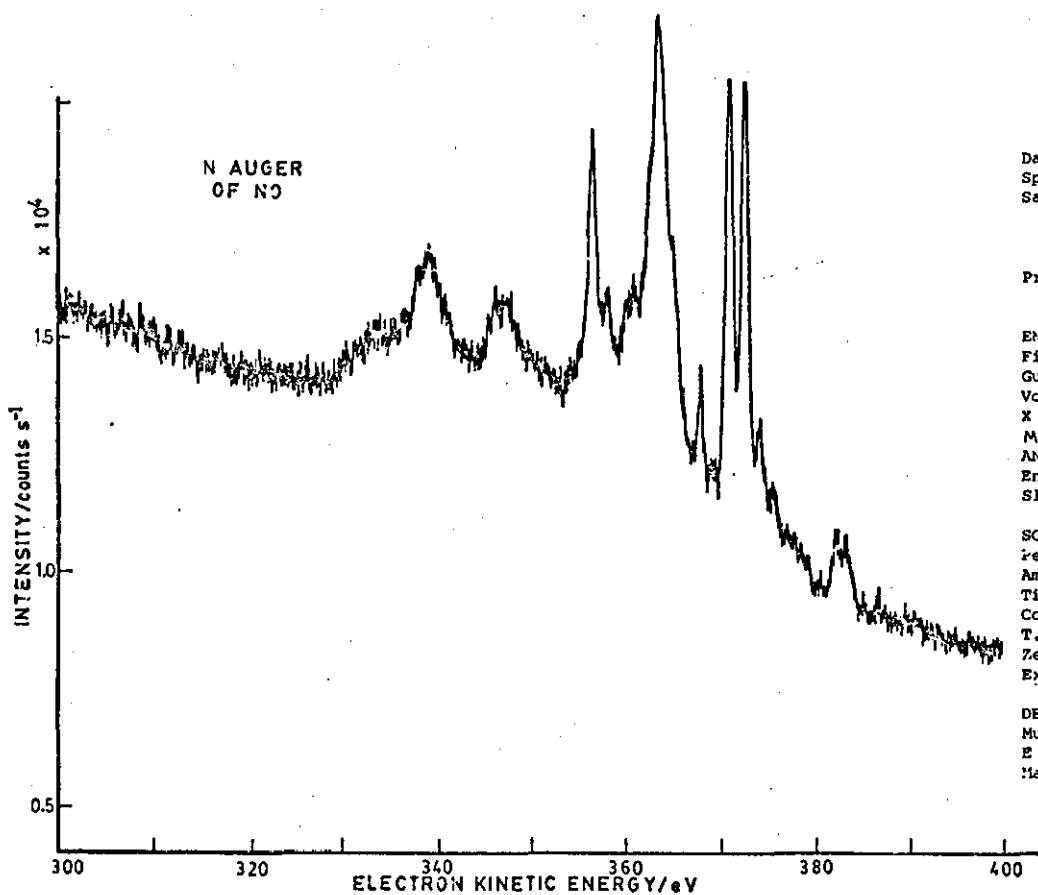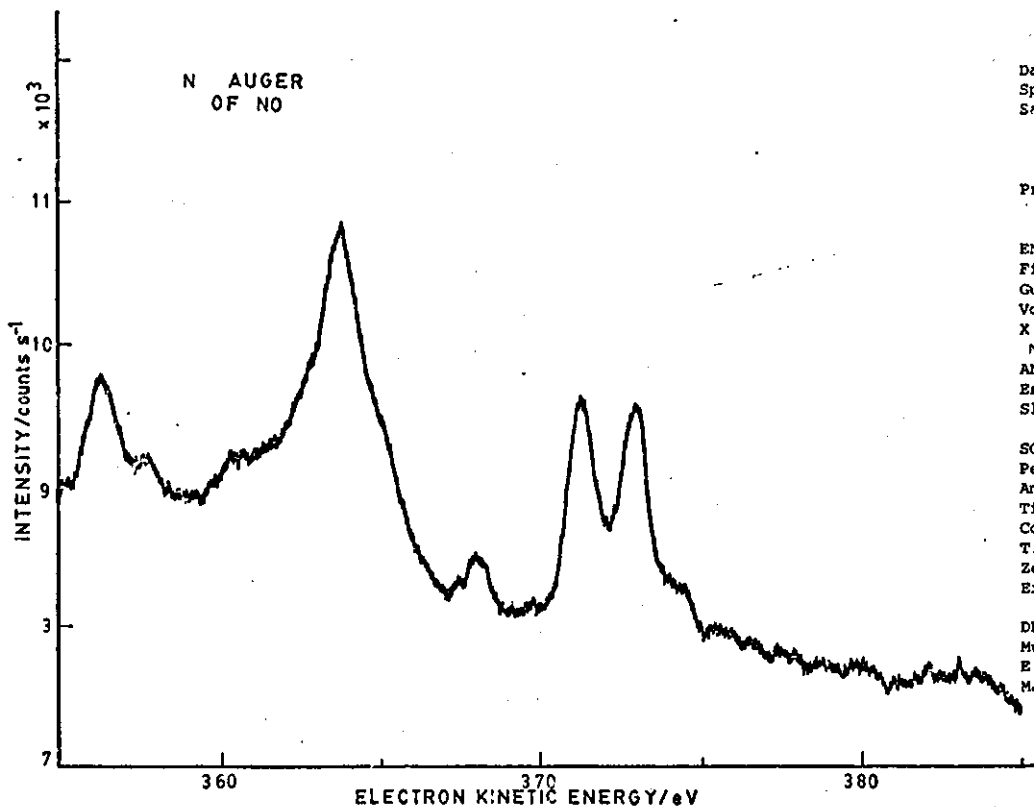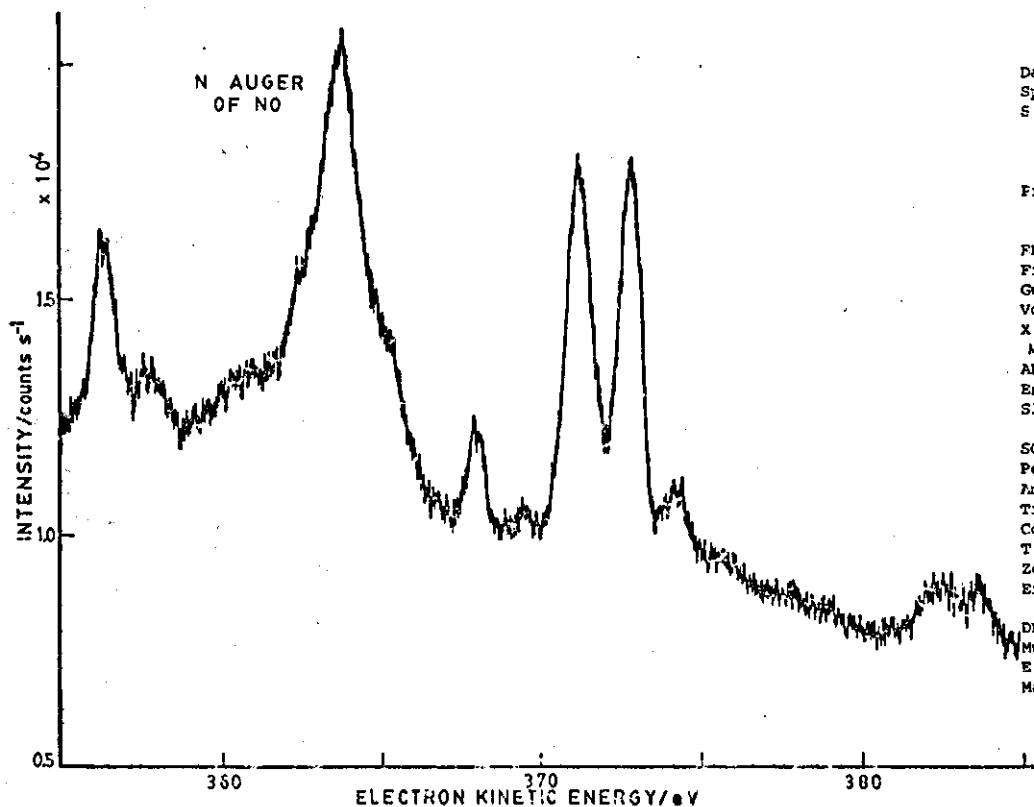ELECTRON KINETIC ENERGY/eV

Date 8/4/78
Spectrum No. 21
Sample
NO ~95%
Ar ~5%
sam 19   t
Press ana   t
gun 2×10⁻⁷ t

ENERGY SOURCE
Fil curr 2.8   A
Gun curr 1   µA
Voltage 5   kV
X 3.44 Y 6.44 F 5.60
Max gun curr 150µA
ANALYZER
Energy 50   V
Slits 2   mm

SCAN
Pedestal 355   V
Amplitude 30   V
Time 300   s
Counts 1×10⁴ s⁻¹
T.C. 3.3   s
Zero supp 0.7
Exp x 3

DETECTOR
Mult 3.2   kV
E Set 100/1000
Mag trim   mA

N AUGER
OF NO

INTENSITY/counts s⁻¹ — × 10⁴

ELECTRON KINETIC ENERGY/eV

Date 24/6/78
Spectrum No. 2
Sample NO
sam 20   t
Press ana 1.2×10⁵ t
gun 2.0×10⁻⁷ t

ENERGY SOURCE
Fil curr 3   A
Gun curr 200   µA
Voltage 5   kV
X 5.52 Y 7.32 F 10
Max gun curr 500µA
ANALYZER
Energy 50   V
Slits 2   mm

SCAN
Pedestal 365   V
Amplitude 30   V
Time 100   s
Counts 1×10⁴ s⁻¹
T.C. 0.33   s
Zero supp 0.5
Exp x 1

DETECTOR
Mult 3.2   kV
E Set 100/1000
Mag trim —   mA

O AUGER
OF NO

Date 24/6/7C
Spectrum No. 3
Sample NO

sam 20 t
Press ana 1.2×10⁻⁶ t
gun 2×10⁻⁷ t

ENERGY SOURCE
Fil curr 3 A
Gun curr 200 μA
Voltage 5 kV
X 5.51 Y 3.32 F 10
Max. gun curr 500μA
ANALYZER
Energy 50 V
Slits 2 mm

SCAN
Pedestal 460 V
Amplitude 100 V
Time 300 s
Counts 1×10⁴ s⁻¹
T.C. 0.33 s
Zero supp —
Exp x —

DETECTOR
Mult 3.2 kV
E Set 100/1000
Mag trim — mA

O AUGER
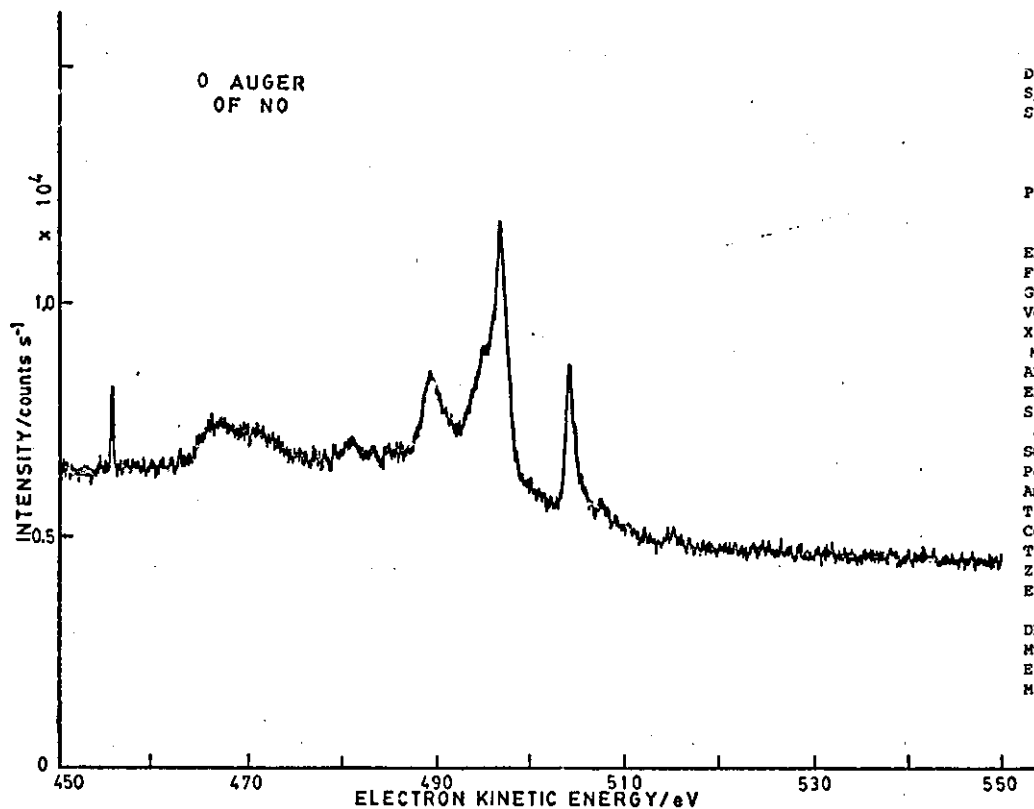OF NO

Date 24/6/78
Spectrum No. 4
Sample NO

nam 20 t
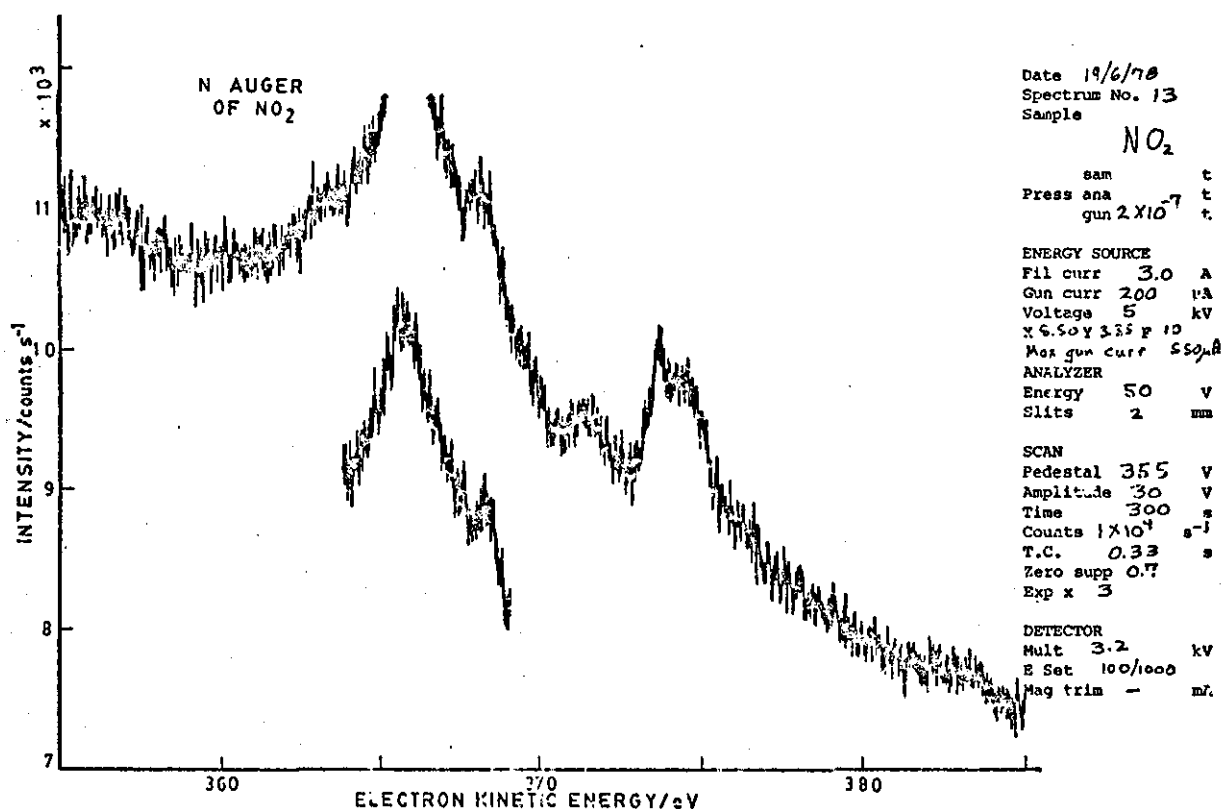Press ana 1.2×10⁻⁵ t
gun 2×10⁻⁷ t

ENERGY SOURCE
Fil curr 3.0 A
Gun curr 200 μA
Voltage 5 kV
X 5.51 Y 3.32 F 10
Max gun curr 500μA
ANALYZER
Energy 50 V
Slits 2 mm

SCAN
Pedestal 480 V
Amplitude 30 V
Time 300 s
Counts 1×10⁴ s⁻¹
T.C. 0.33 s
Zero supp —
Exp x —

DETECTOR
Mult 3.2 kV
E Set 100/1000
Mag trim — mA

N AUGER
OF NO₂

ARGON

INTENSITY/counts s⁻¹

ELECTRON KINETIC ENERGY/eV

Date 14/6/78
Spectrum No. 3
Sample NO₂
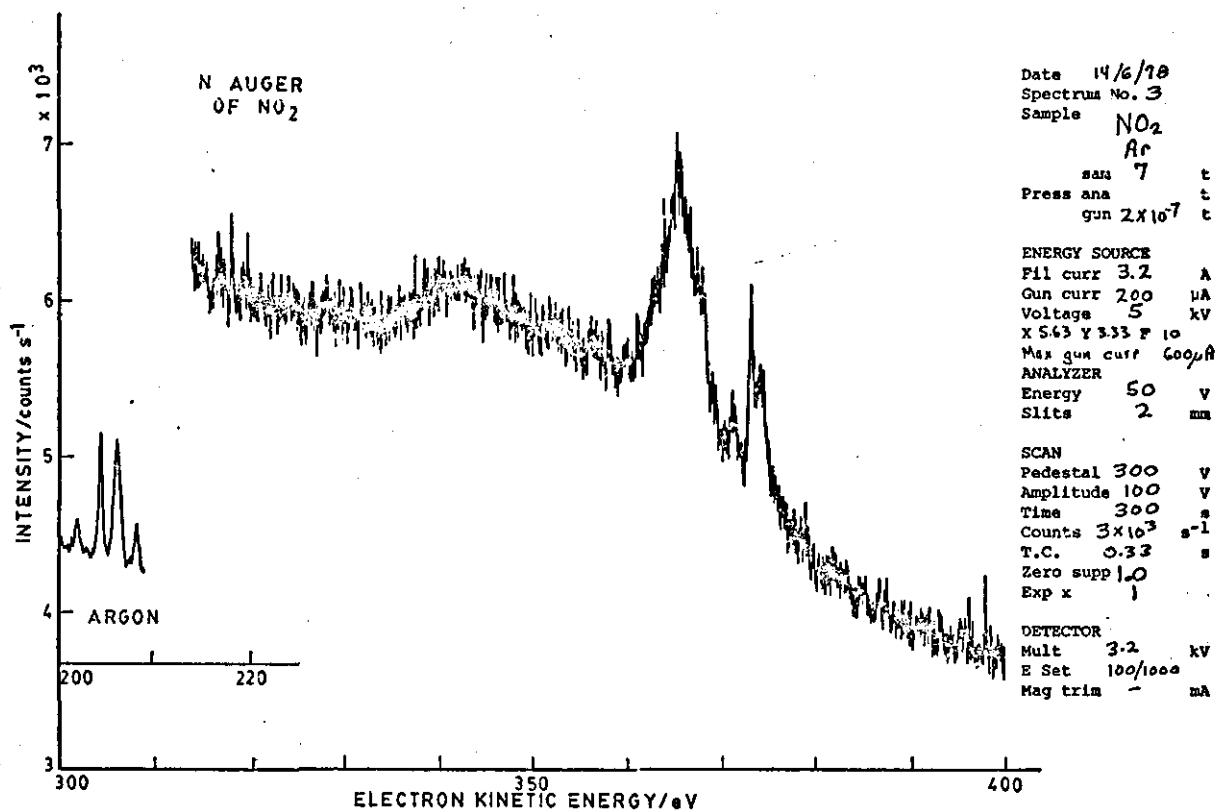Ar
sam 7 t
Press ana t
gun 2 X 10⁻⁷ t

ENERGY SOURCE
Fil curr 3.2 A
Gun curr 200 µA
Voltage 5 kV
X 5.63 Y 3.33 F 10
Max gun curr 600µA
ANALYZER
Energy 50 V
Slits 2 mm

SCAN
Pedestal 300 V
Amplitude 100 V
Time 300 s
Counts 3 x 10³ s⁻¹
T.C. 0.33 s
Zero supp 1.0
Exp x 1

DETECTOR
Mult 3.2 kV
E Set 100/1000
Mag trim — mA

N AUGER
OF NO₂

INTENSITY/counts s⁻¹

ELECTRON KINETIC ENERGY/eV

Date 19/6/78
Spectrum No. 13
Sample
NO₂
sam t
Press ana t
gun 2 X 10⁻⁷ t

ENERGY SOURCE
Fil curr 3.0 A
Gun curr 200 µA
Voltage 5 kV
X 5.50 Y 3.35 F 10
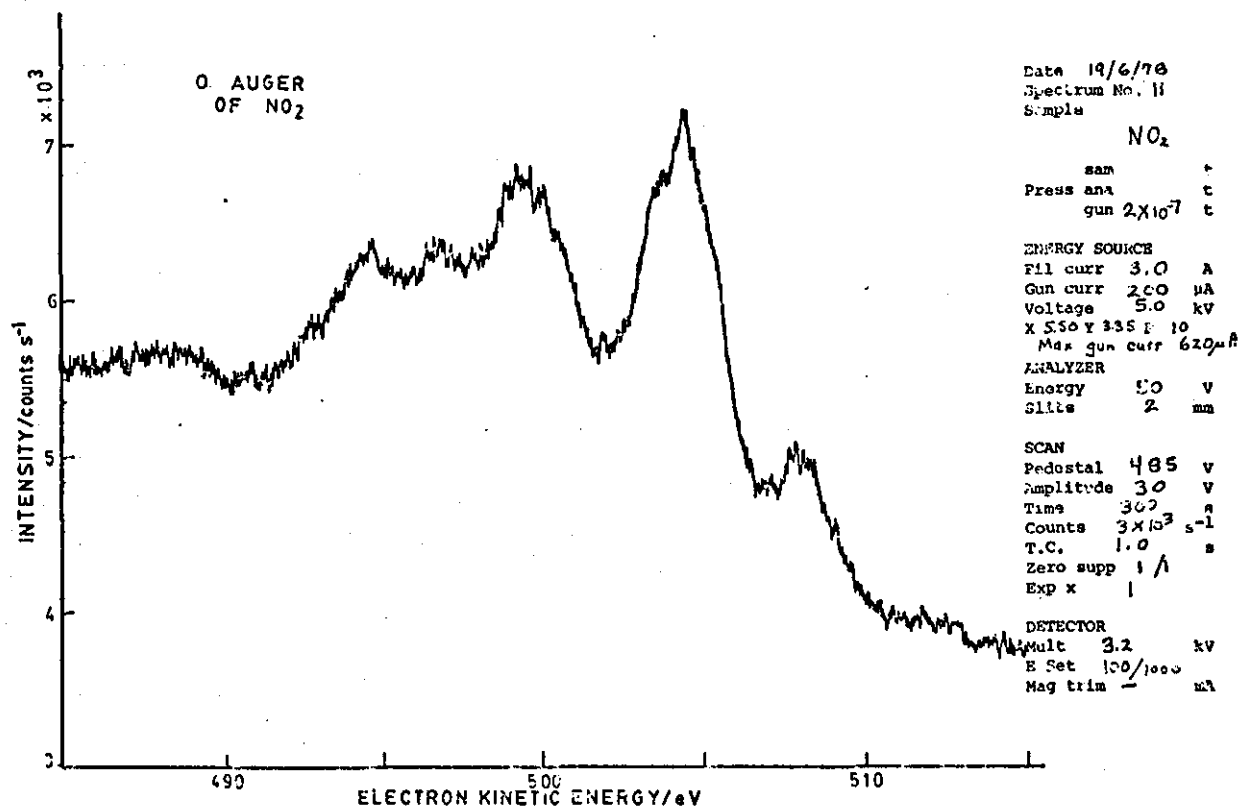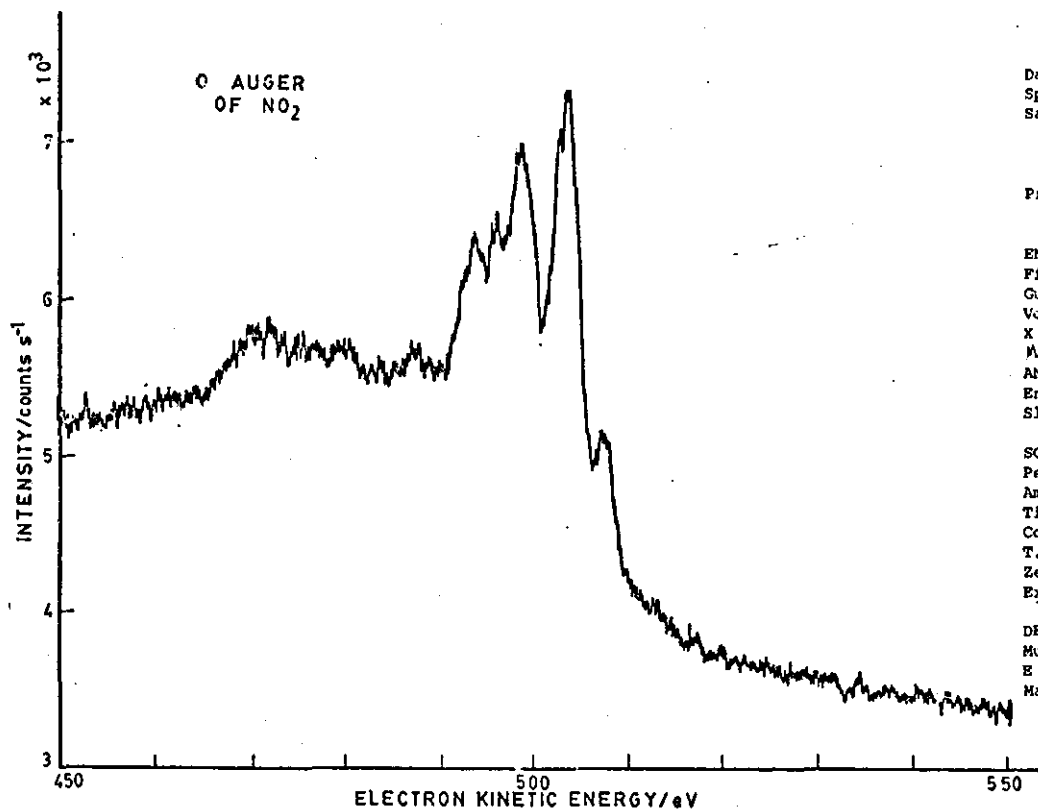Max gun curr 550µA
ANALYZER
Energy 50 V
Slits 2 mm

SCAN
Pedestal 355 V
Amplitude 30 V
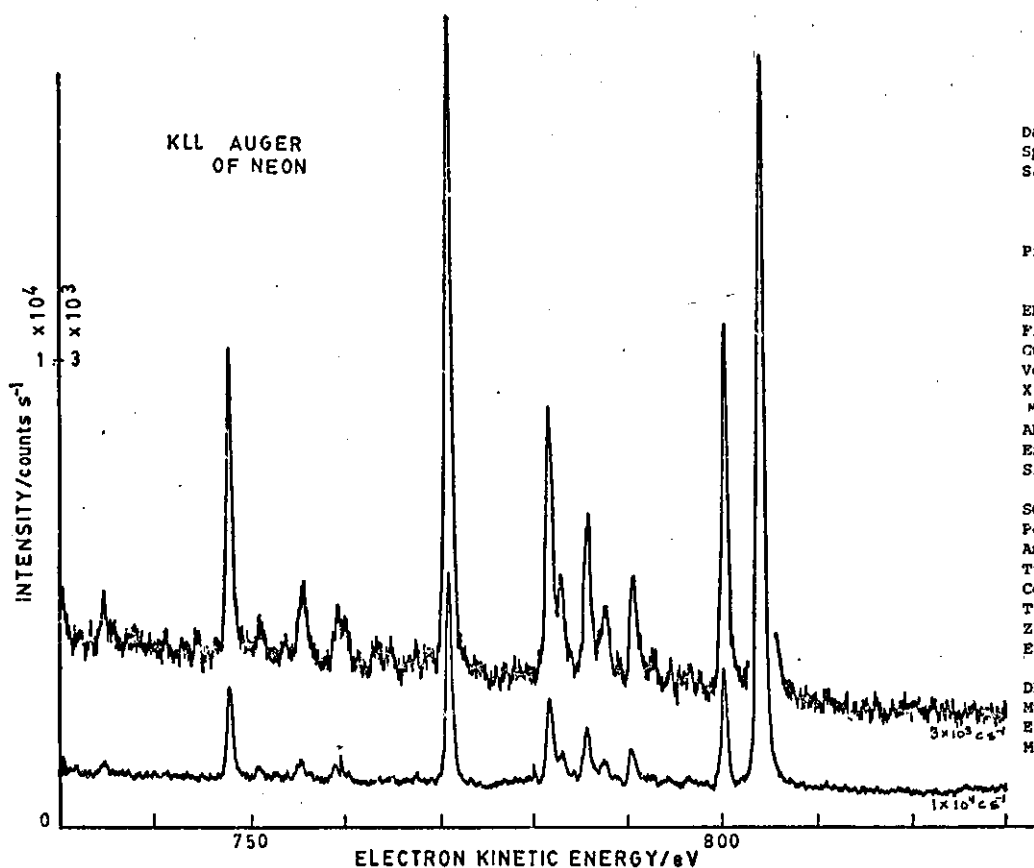Time 300 s
Counts 1 X 10⁴ s⁻¹
T.C. 0.33 s
Zero supp 0.7
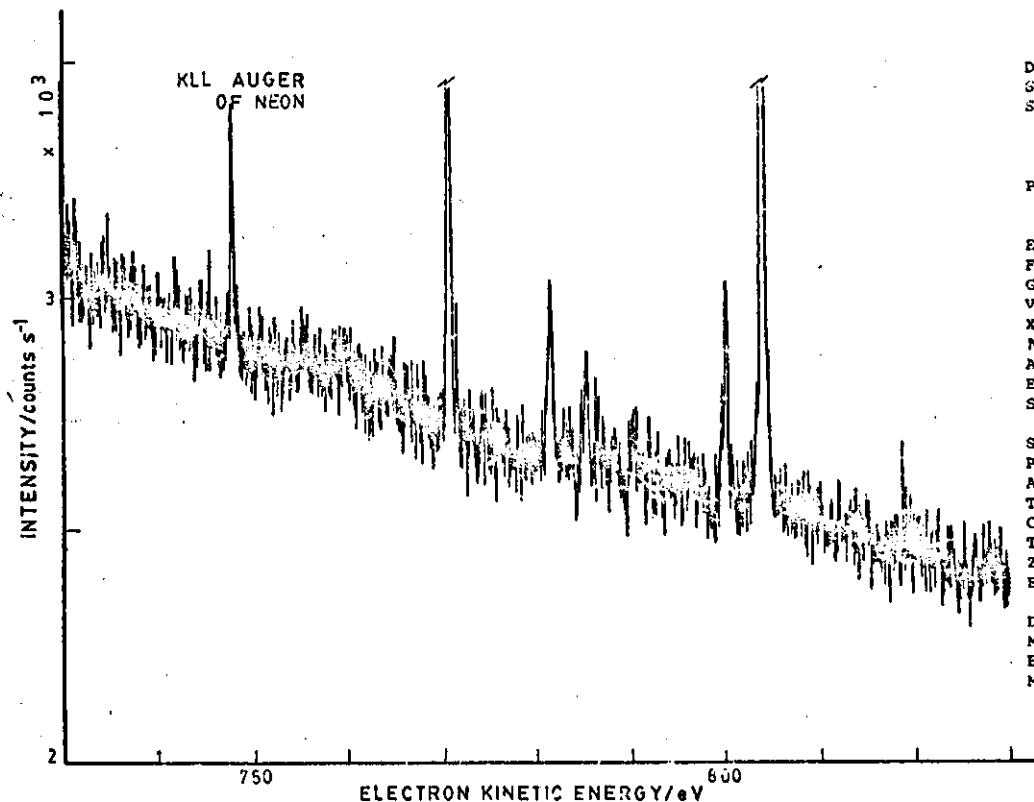Exp x 3

DETECTOR
Mult 3.2 kV
E Set 100/1000
Mag trim — mA

O AUGER OF NO₂

Date 19/6/76
Spectrum No. 10
Sample NO₂

sam t
Press ana t
gun 2×10⁻⁷ t

ENERGY SOURCE
Fil curr 3.0 A
Gun curr 2.00 µA
Voltage 5 kV
X 5.50 Y 3.35 F 10
Max gun curr 650µA
ANALYZER
Energy 50 V
Slits 2 mm

SCAN
Pedestal 450 V
Amplitude 100 V
Time 300 s
Counts 3×10³ s⁻¹
T.C. 0.33 s
Zero supp 1/1
Exp x 1

DETECTOR
Mult 3.2 kV
E Set 100
Mag trim — mA

O AUGER OF NO₂

Date 19/6/76
Spectrum No. 11
Sample NO₂

sam t
Press ana t
gun 2×10⁻⁷ t

ENERGY SOURCE
Fil curr 3.0 A
Gun curr 2.00 µA
Voltage 5.0 kV
X 5.50 Y 3.35 F 10
Max gun curr 620µA
ANALYZER
Energy 50 V
Slits 2 mm

SCAN
Pedestal 485 V
Amplitude 30 V
Time 300 s
Counts 3×10³ s⁻¹
T.C. 1.0 s
Zero supp 1/1
Exp x 1

DETECTOR
Mult 3.2 kV
E Set 100/1000
Mag trim — mA

KLL AUGER
OF NEON

Date 28/4/78
Spectrum No. 4
Sample
        Ne

        sam   13   t
Press ana   t
        gun 2×10⁻⁷   t

ENERGY SOURCE
Fil curr   3.4   A
Gun curr   200   μA
Voltage   5   kV
X 2.70 Y 5.87 P 10
Max gun current 245μA
ANALYZER
Energy   50   V
Slits   2   mm

SCAN
Pedestal   730   V
Amplitude 100   V
Time   300   s
Counts 1×10⁴/3×10³ s⁻¹
T.C.   0.33   s
Zero supp -
Exp x   -

DETECTOR
Mult   3.2   kV
E Set   100/1000
Mag trim   -   mA

KLL AUGER
OF NEON

Date   19/6/78
Spectrum No. 3
Sample
        Ne

        sam   20   t
Press ana   t
        gun 2×10⁻⁷   t

ENERGY SOURCE
Fil curr   3.0   A
Gun curr   200   μA
Voltage   5   kV
X 5.45 Y 3.25 P 10
Max gun curr 600μA
ANALYZER
Energy   20   V
Slits   2   mm

SCAN
Pedestal   730   V
Amplitude 100   V
Time   300   s
Counts 1×10³ s⁻¹
T.C.   0.33   s
Zero supp 1/1
Exp x   1

DETECTOR
Mult   3.2   kV
E Set   100/1000
Mag trim   mA

S AUGER OF H₂S

S AUGER OF H₂S

S AUGER
OF H₂S

$\times 10^4$

INTENSITY/counts s⁻¹

11

10

9

8

7

120   130   140   150
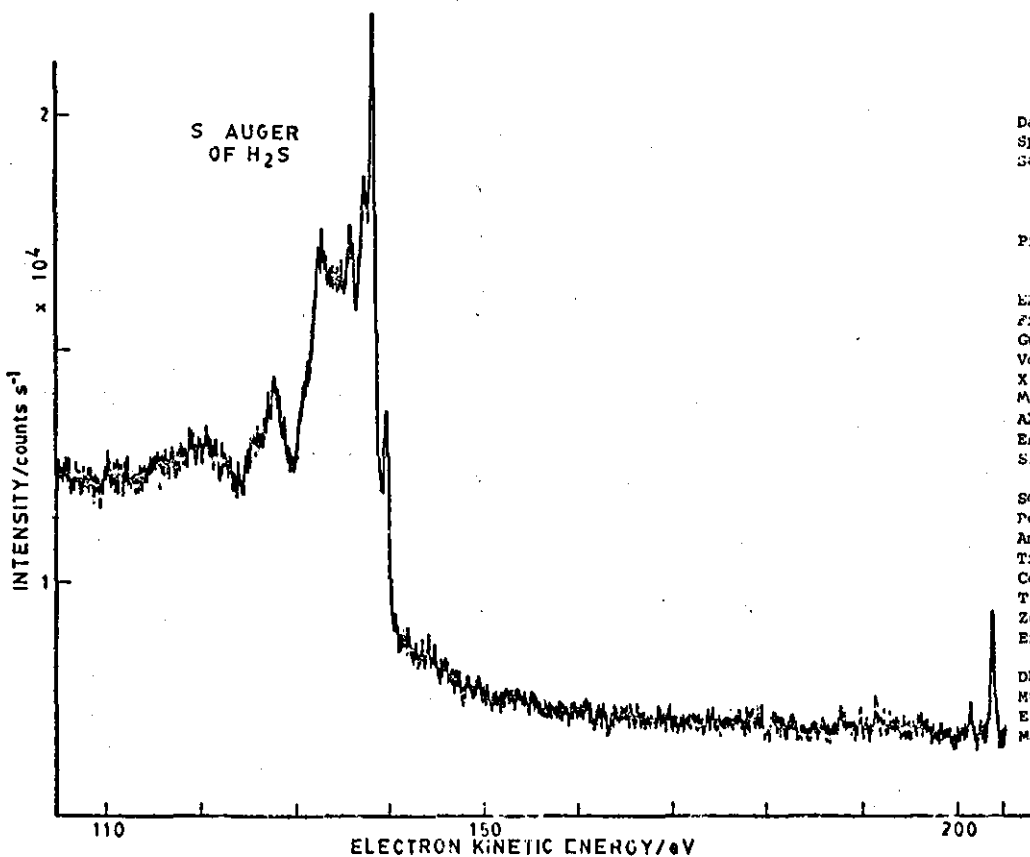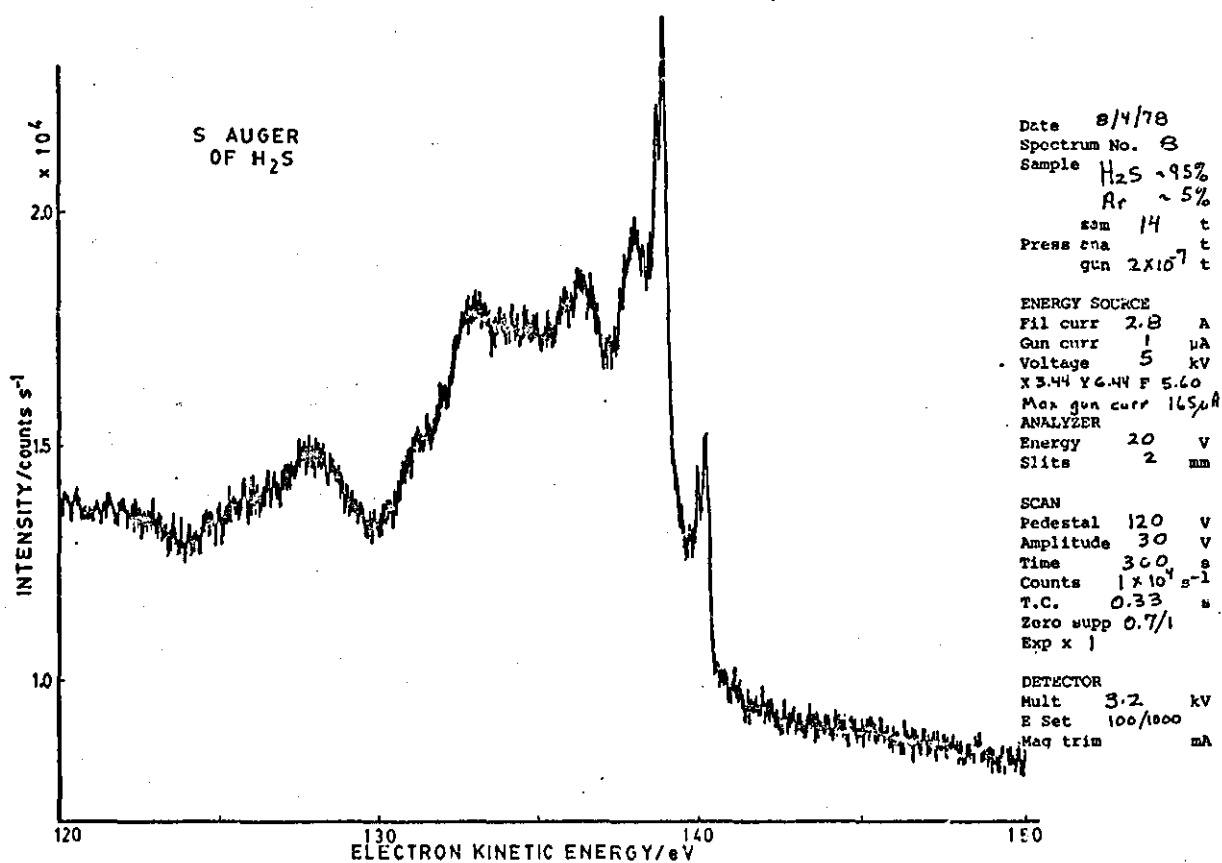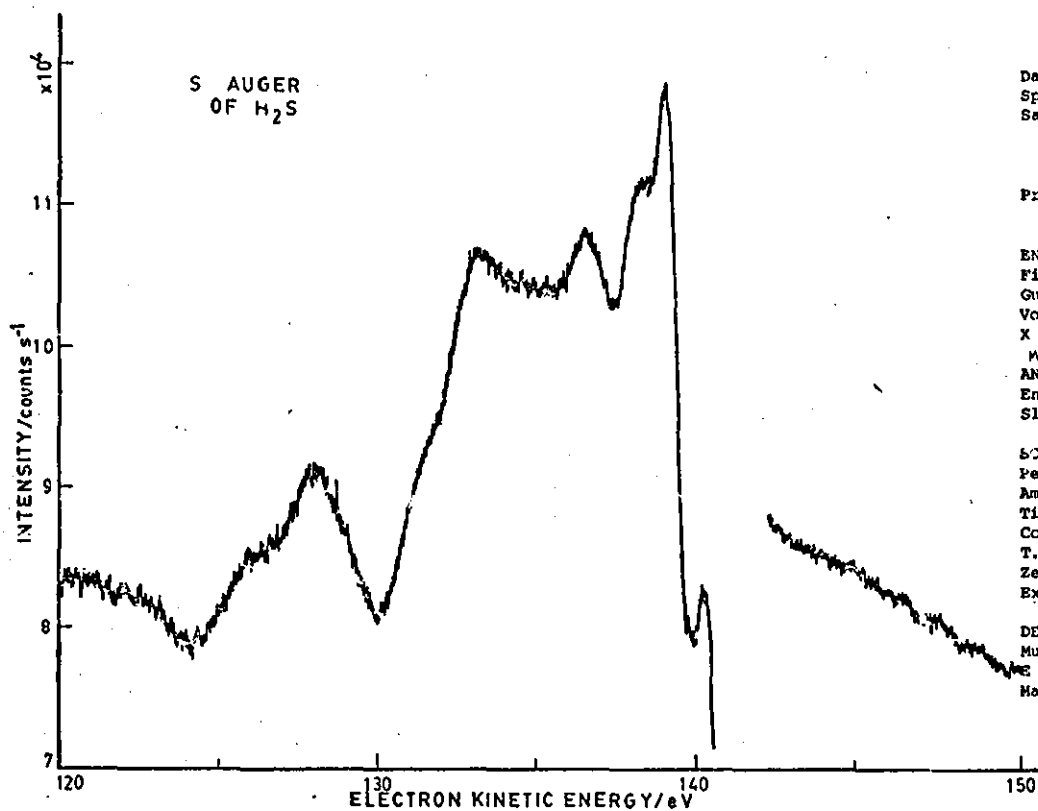ELECTRON KINETIC ENERGY/eV

Date 8/4/78
Spectrum No. 7
Sample
    H₂S ~95%
    Ar ~ 5%
    sam 14.5   t
Press ana   t
    gun 2×10⁻⁷ t

ENERGY SOURCE
Fil curr 2.8   A
Gun curr   1   µA
Voltage   5   kV
X 3.44 Y 6.44 F 5.60
 Max gun curr 165µA
ANALYZER
Energy   50   V
Slits   2   mm

SCAN
Pedestal 120   V
Amplitude 30   V
Time   300   s
Counts   1×10⁵ s⁻¹
T.C.   0.33 s
Zero supp 0.7/1
Exp x   3

DETECTOR
Mult   3.2   kV
E Set   100/1000
Mag trim   mA

S AUGER
OF H₂S

$\times 10^4$

2.0

INTENSITY/counts s⁻¹

1.5

1.0

120   130   140   150
ELECTRON KINETIC ENERGY/eV

Date 8/4/78
Spectrum No. 8
Sample H₂S ~95%
        Ar ~5%
    sam 14   t
Press ana   t
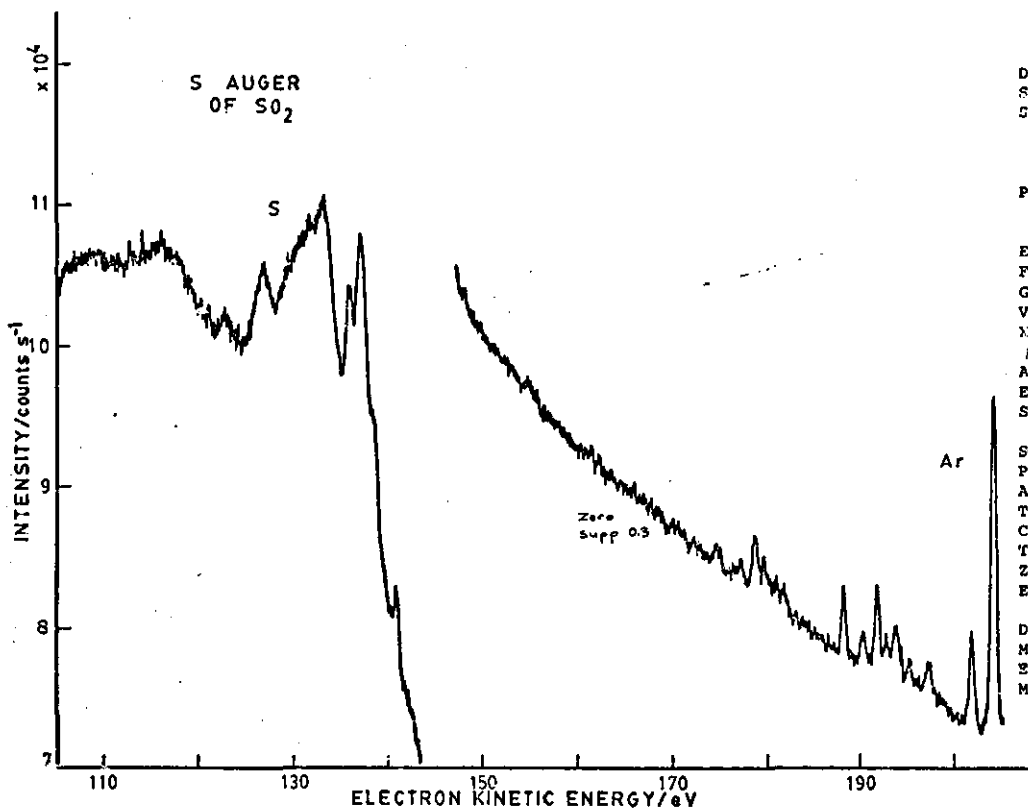   gun 2×10⁻⁷ t

ENERGY SOURCE
Fil curr 2.8   A
Gun curr   1   µA
Voltage   5   kV
X 3.44 Y 6.44 F 5.60
Max gun curr 165µA
ANALYZER
Energy   20   V
Slits   2   mm

SCAN
Pedestal 120   V
Amplitude 30   V
Time   300   s
Counts   1×10⁴ s⁻¹
T.C.   0.33 s
Zero supp 0.7/1
Exp x   1

DETECTOR
Mult   3.2   kV
E Set   100/1000
Mag trim   mA

S AUGER
OF SO₂

S

Ar

Zero
supp 0.3

INTENSITY/counts s⁻¹

×10⁴

11

10

9

8

7

110   130   150   170   190

ELECTRON KINETIC ENERGY/eV

Date   6/4/78
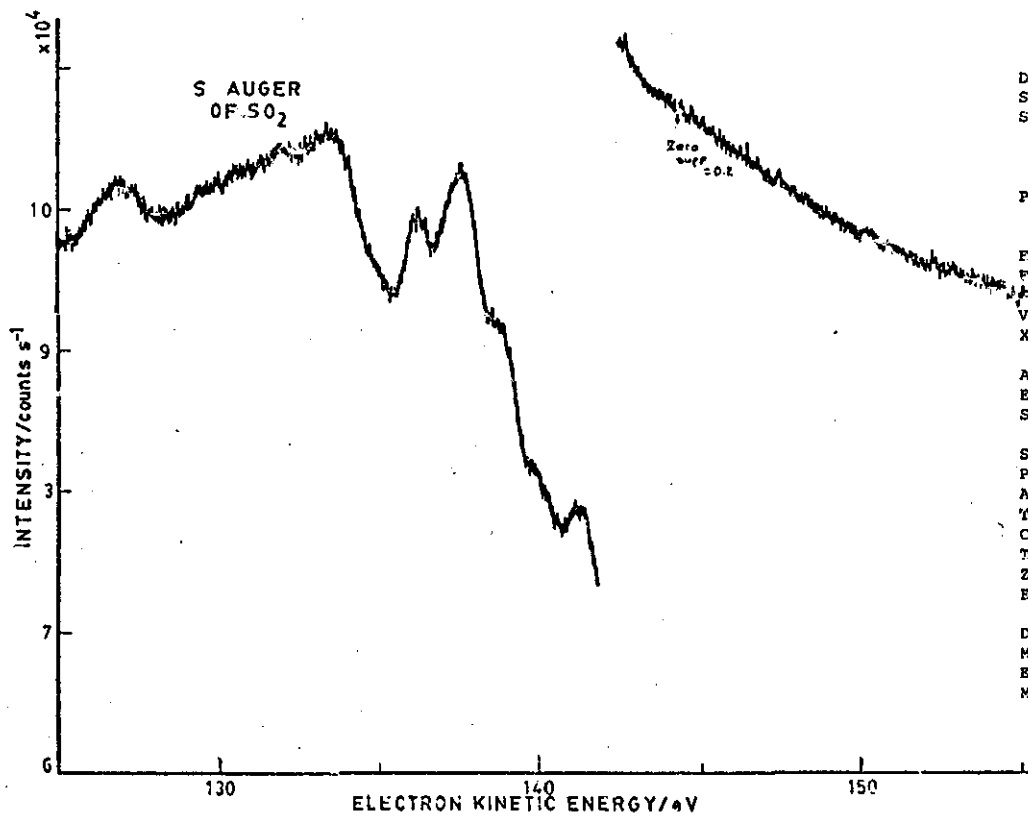Spectrum No. 2
Sample
        SO₂ ·95%
        Ar ~ 5%
        sam 20   t
Press ana   t
        gun 2×10⁻⁷ t

ENERGY SOURCE
Fil curr   2.8   A
Gun curr   1   µA
Voltage   5   kV
X 3.50 Y 640 F 5.67
Max gun curr 220µA
ANALYZER
Energy   50   V
Slits   2   mm

SCAN
Pedestal   105   V
Amplitude 100   V
Time   300   s
Counts   1×10⁵ s⁻¹
T.C.   0.33   s
Zero supp 0.7
Exp x   3

DETECTOR
Mult   3.2   kV
E Set   100
Mag trim   -   nA

S AUGER
OF SO₂

Zero
supp 0.2

INTENSITY/counts s⁻¹

×10⁴

10

9

8

7

6

130   140   150

ELECTRON KINETIC ENERGY/eV

Data   6/4/78
Spectrum No. 3
Sample
        SO₂ ·95%
        Ar ~ 5%
        sam 19   t
Press ana   t
        gun 2×10⁻⁷ t

ENERGY SOURCE
Fil curr   2.8   A
Gun curr   1   µA
Voltage   5   kV
X 3.50 Y 640 F 5.67
Max gun curr 200µA
ANALYZER
Energy   50   V
Slits   2   mm

SCAN
Pedestal   125   V
Amplitude 30   V
Time   300   s
Counts   1×10⁵ s⁻¹
T.C.   0.33   s
Zero supp 0.6
Exp x   3

DETECTOR
Mult   3.2   kV
E Set   100
Mag trim   mA

Cl AUGER
OF CCl$_4$
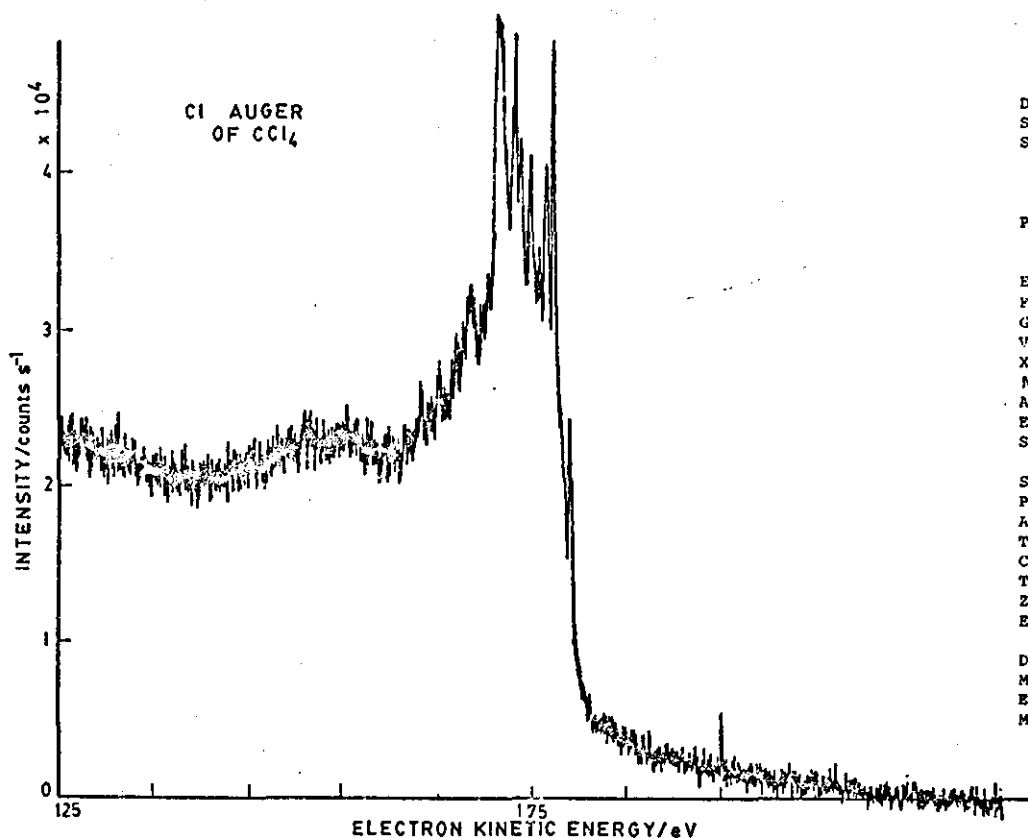
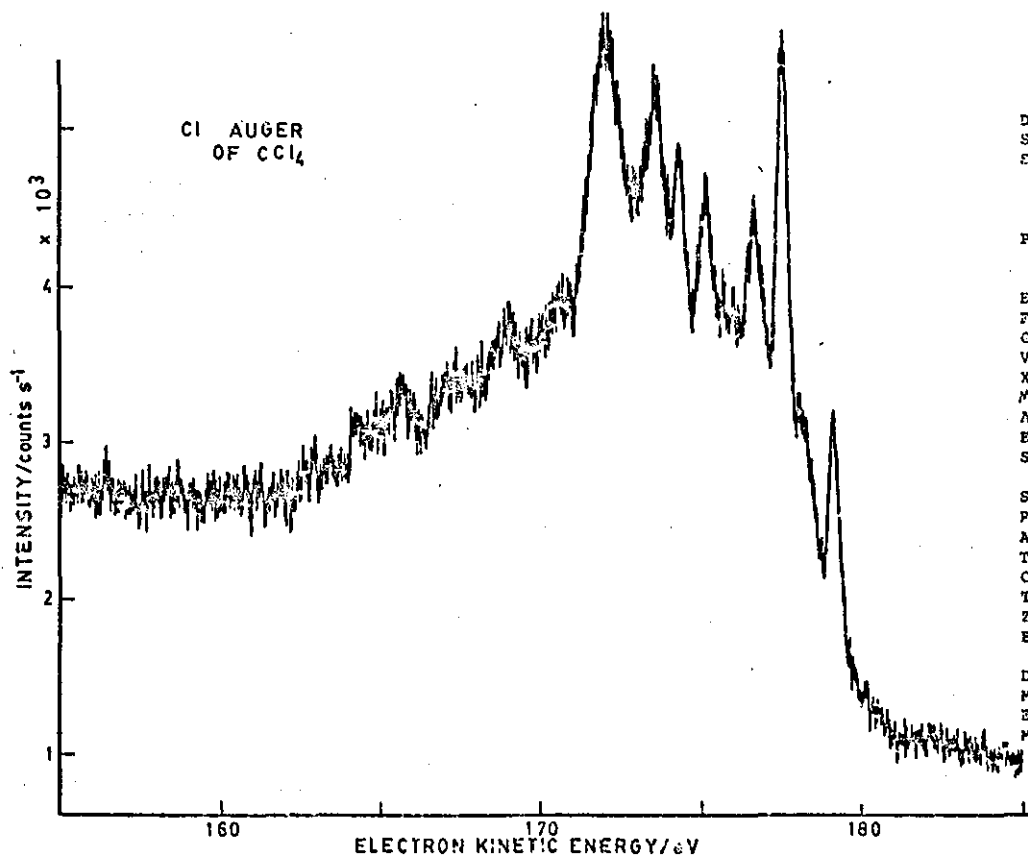Date 10/5/78
Spectrum No. 5
Sample
CCl$_4$

sam 18 t
Press ana t
gun 2x10^{-7} t

ENERGY SOURCE
Fil curr 3.4 A
Gun curr 200 μA
Voltage 5 kV
X 2.75 Y 5.80 F 10
Max gun curr 210μA
ANALYZER
Energy 20 V
Slits 2 mm

SCAN
Pedestal 125 V
Amplitude 100 V
Time 300 s
Counts 3 x 10^4 s^{-1}
T.C. 0.33 s
Zero supp —
Exp x —

DETECTOR
Mult 3.2 kV
E Set 100/1000
Mag trim — mA

Cl AUGER
OF CCl$_4$
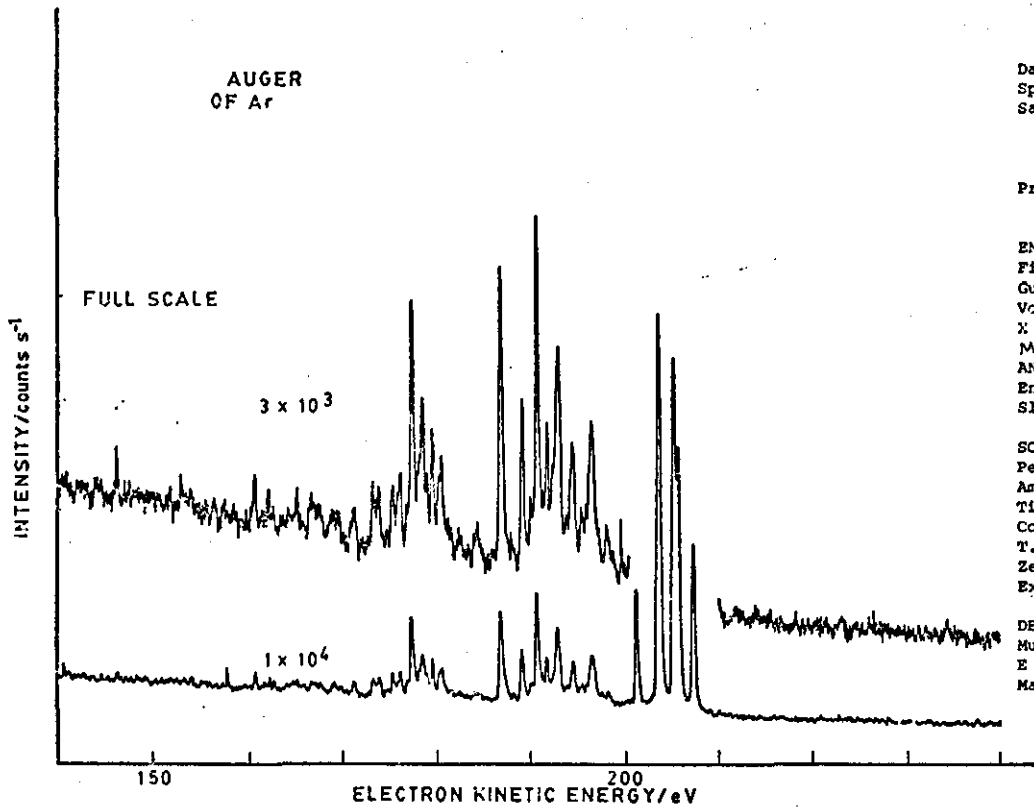
Date 10/5/78
Spectrum No. 6
Sample
CCl$_4$

sam 18 t
Press ana t
gun 2x10^{-7} t

ENERGY SOURCE
Fil curr 3.4 A
Gun curr 200 μA
Voltage 5 kV
X 2.75 Y 5.80 F 10
Max gun curr 210μA
ANALYZER
Energy 20 V
Slits 2 mm

SCAN
Pedestal 155 V
Amplitude 30 V
Time 300 s
Counts 3 x 10^3 s^{-1}
T.C. 0.33 s
Zero supp 0.2/1
Exp x 1

DETECTOR
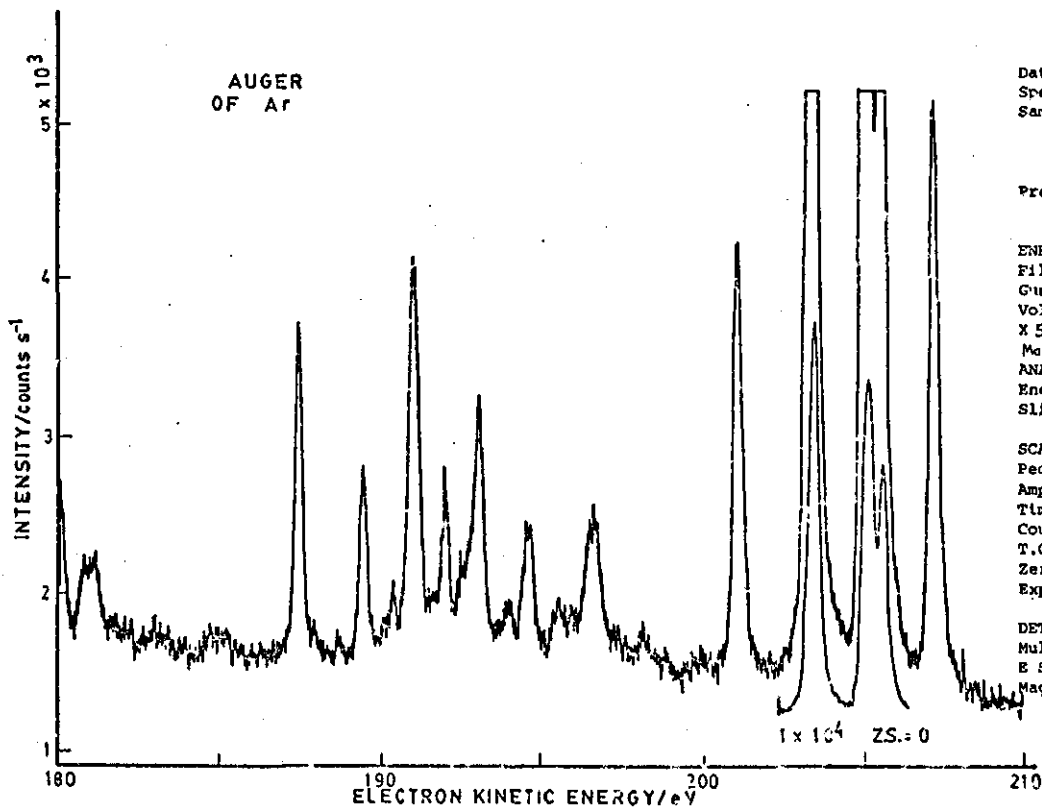Mult 3.2 kV
E Set 100/1000
Mag trim — mA

AUGER
OF Ar

FULL SCALE

3×10^3

1×10^4

INTENSITY/counts s^{-1}

150   200

ELECTRON KINETIC ENERGY/eV

Date 19/6/78
Spectrum No. 5
Sample   Ar

         sam 20   t
Press ana   t
         gun 2×10^{-7} t

ENERGY SOURCE
Fil curr 3.0   A
Gun curr 100   µA
Voltage   5   kV
X 5.46 Y 3.25 F 10
Max gun curr 700µA
ANALYZER
Energy   20   V
Slits   2   mm

SCAN
Pedestal 140   V
Amplitude 100   V
Time   300   s
Counts   1×10^4 s^{-1}
T.C.   0.33   s
Zero supp —
Exp x   —

DETECTOR
Mult 3.2   kV
E Set 100/1000
Mag trim —   mA

5×10^3

AUGER
OF Ar

INTENSITY/counts s^{-1}

1×10^4 ZS. 0

180   190   200   210

ELECTRON KINETIC ENERGY/eV

Date 19/6/78
Spectrum No. 6
Sample   Ar

         sam 20   t
Press ana   t
         gun 2×10^{-7} t

ENERGY SOURCE
Fil curr 3.0   A
Gun curr 100   µA
Voltage   5   kV
X 5.45 Y 3.25 F 10
Max gun curr 700µA
ANALYZER
Energy   20   V
Slits   2   mm

SCAN
Pedestal 180   V
Amplitude 30   V
Time   300   s
Counts   3×10^3 s^{-1}
T.C.   0.33   s
Zero supp 0.2/1
Exp x   1

DETECTOR
Mult 3.2   kV
E Set 100/1000
Mag trim   mA