WATER
WATER
WATER
WATER
WATER
WATER
WATER
WATER
WATER
WATER

PROJECT COMPLETION
REPORT NO. 398X

Determination of Trace Metal Pollutants in Water Resources and Stream Sediments

By
Charles R. Cothern
University of Dayton
1972

United States Department
of the Interior

CONTRACT NO.
A-019-OHIO
14-01-0001-3535

State of Ohio
Water Resources Center
Ohio State University

Determination of Trace Metals Pollutants in Water Resources Using X-ray Fluorescence

OWRR Project No. A-019-OHIO

Annual Allotment Grant Agreement
No. 14-31-0001-3225

Report Covers Work Done Between
July 1, 1970 and June 30, 1971

C. R. Cothern
University of Dayton
Physics Department
Dayton, Ohio

General Synopsis

The present two reports covering the period July 1, 1970 to June 30, 1972 involve the examination and determination of a number of the characteristics of the technique of X-ray fluorescence. This study is part of an overall program in our laboratory to address the general problem of the determination of trace metals in environmental samples.

Many of the pollutants in our environment can be easily detected. For example, smoke from chimneys, discoloration or smell of rivers, noise in urban areas. However many substances are being added to our environment by men which are both harmful to life and undetectable by the human senses. That is, they are undetectable until the effects are noticed which is often too late. It is thus important to develop analytical techniques capable of determining the presence of these non-visable pollutants. The thrust of the present work is to investigate and develop the method of X-ray fluorescence (XRF) as a routine method for determining the presence of trace metals in environmental samples particularly water and sediment samples.

Some of the advantages of XRF compared to other techniques for trace metal determinations are; the method is non-destructive, that is the sample is unaltered by the examination performed; the data alalysis is simple and can be easily computerized; in addition the technique can be automated removing the need for a full-time technician to run the tests; this method determines the presence of a wide range of metals simultaneously and the method is potentially portable, that is in the near future field units weighing about 30 lbs. can be constructed.

The present work has demonstrated the linearity, reproducibility and reliability of XRF. A method for quantitatively calibrating the equipment involved has been developed. This proceedure involves vacuum depositing known amounts of metals to manufacture standards. Further refinements of this method will produce a quick, reliable check of the analytical precision of the method. It is shown that the sensitivity of XRF is suitable for most environmental problems. As a demonstration of the applicability of XRF a study of the water and sediments in the Great Miami River in Dayton, Ohio has been conducted. This study revealed that in general the pollution in the river was below accepted federal and state standards for maximum concentration.

The major problem area for XRF requiring more investigation is the effect on quantitative determination of metals of the thickness and composition of the sample. The sample itself can alter the incoming (probing) radiations and the outgoing (indicator) radiations. Some subtle effects have been found and proceedures for eliminating these problems have been, in part, developed. Further study is needed in this area and is being pursued in our laboratory.

The most valuable assets of the XRF technique lie in the speed one uses for determining the presence of a large number of elements simultaneously and the potential portability of the instrumentation.

This report contains two sections. These two sections represent the final report for work done between July 1, 1970 and June 30, 1972. The first section describes work done in the first year (July 1, 1970 to June 30, 1971) and the second section covers work done in the second year (July 1, 1971 to June 30, 1972). The tables of contents for each section can be found at the beginning of the corresponding section.

Table of Contents

Personnel Involved in this Project

Principal Investigator

C. R. Cothern, Ph. D.

Student Research Assistants

M. B. Blasius
T. R. Dittrich
C. M. Kessler
S. J. Kerkhoff
A. L. Sagle
R. S. Wright

Student Assistants

C. D. Brown
C. Henry
J. Krayer
T. Rogers
M. Schaftner
T. Schmitt
S. Stoner

Research Consultants

J. A. Deye, Ph. D.
J. Walker, Jr., M. S.

Figures

Tables

Abstract

Trace metals collected on small pore filter paper (0.45 microns) and ion exchange filter paper by allowing samples (300-500 ml) of water to pass through these filter papers were analyzed by the X-ray fluorescence method. The procedures necessary for using the X-ray fluorescence method are described as well as modifications possible for special problem situations. A number of outfalls on the Great Miami River were sampled over one year showing the presence of the following metals, Ca, Ti, Cr, Fe, Cu, Zn, Sr, Cd, and Cr. Elements in the periodic table between Ti and Cs were seen to a sensitivity limit of the order of 30 ppb.

I. Introduction

The increased emphasis on water pollution control indicates the need for improved methods of analyzing water samples (A-6). Although a detailed discussion of all the analytical methods for determining the presence of trace metals in aquatic samples is not the object of this paper, a few comments will be made regarding their relative merits. For further information the reader is referred to a recent review article (M-7 & W-3).

The analytical tools with trace metal sensitivities comparable to or better than that of X-ray fluorescence (XRF) include atomic absorption (AA), neutron activation analysis (NAA), and emission spectroscopy (ES). In some special cases, e.g. using AA to measure the presence of Hg or using NAA to measure the presence of Si, a particular method is superior; but, in general all these methods are capable of measurement in the parts per million and in some cases the sub-parts per million range. Table I indicates some of the relative advantages of these methods. Although none of these methods are portable at present, the future holds promise for XRF and NAA (it should be noted that portable XRF instruments are available now for determination of a single element) (B-6). NAA presently requires a large nuclear reactor (the minimum flux for best overall performance is around 10^{12} neutrons/sec/cm^2) (G-8) but the future availability of ^{252}Cf (C-8) should provide adequate portable activation sources. It is not unreasonable to expect that present solid state X-ray detectors used in XRF will become portable in the future (M-5). The only present difficulty in making these units portable is that they require cooling to liquid nitrogen temperature. A portable unit would weigh only 10 to 20 pounds (K-10) and could rapidly determine in the field the presence of many metals in water samples.

TABLE I

Method		Data Analysis Simple	Non Destructive	Detect All Metals Simultaneously	Portability	Automated
Atomic Absorption		X				X
Neutron Activation Analysis			X	X	X	
Optical Emission Spectroscopy		X				
X-ray Fluorescence		X	X	X	X	X

Data analysis for XRF is less complicated than analyzing the gamma ray spectrum of NAA. The NAA energy spectrum contains ten or more peaks per element. Also the identification of elements in NAA spectra requires both intensity and half-life information. This requires the resolving and analysis of several complex spectra.

Only two of the above methods (XRF and AA) are instrumented in such a way that they can be automated. In the AA method the samples to be tested are poured into sample tubes and placed in a large rack, containing as many as 200 tubes. In XRF the filter paper on which the sample is collected is placed in a holder for immediate analysis. The complete analysis in both cases can be computerized. If the samples have to be shipped over large distances, the paper filters used in XRF have obvious advantages over the liquids used in AA.

One of the major problems with analysis of trace metals at present is the non-uniformity of results from both different techniques and different laboratories. In an effort to standardize the present techniques and laboratories, the National Bureau of Standards is providing standardized materials (N-2). At present they provide orchard leaves which contain several trace metals of known quantities. In the near future, they will also provide samples of beef livers. The amount of trace metals in these standards are determined by at least three independent analytical techniques. In the need for independent methods X-ray fluorescence is a very valuable tool, since for many metals finding as many as three in dependent analytical methods is difficult.

The primary motivation for studying trace metals in water resources is the effect they have on human beings who consume them. Although most metals are not toxic in trace amounts, several do have deliterious effects. These effects are discussed in some detail in Chapter II of this report.

A discussion of the X-ray fluorescence technique, apparatus and some of the problems encountered by this method are discussed in Chapter III. Also included is a discussion of the use of ion exchange filter papers.

A description of the experimental procedures and techniques used in the present work is given in Chapter IV. This includes information concerning the accuracy and sensitivity of X-ray fluorescence. Also included in this chapter are the results of a trace metal survey of the Great Miami River.

The last Chapter, Chapter V, includes discussion and conclusions from the present work and possible areas that require further work in the future.

II. Health Effects of Trace Metals

A. General

The trace elements necessary to life on earth are more important to the existance of that life than their organic micronutrient counterparts, vitamins. The elements cannot be synthesized as vitamins can, but must exist in a narrow range of concentration in the environment to support life. Both deficiencies and excesses of trace elements can kill (S-1). The only source of trace elements is the earth's crust and sea water, and without them life would cease to exist.

A trace element can be defined as one making up less than 0.01 percent of the organism being considered. Because of the abundance of low atomic number (Z) elements in the earth's crust, it is not surprising that more than 99% of the structure of living things is composed of 12 of the first 20 elements in the periodic table. In spite of their miniscule presence in the human body, trace metals play an important role in human existance and can cause harmful effects. For example tiny amounts of iron are essential to the construction of hemoglobin in our blood to carry oxygen while only 50 parts per billion of mercury can cause harmful effects in humans.

The extreme biological consequences of even small changes in the concentrations of trace elements as well as the very small amounts which are required suggests that their action can only be that of vital links in the enzyme systems (D-1); e.g. iron in hemoglobin, copper in ascorbic acid oxidase, zinc in carbonic anhydrase. With many metals present one may substitute for another preventing proper physiological mechanisms to function.

Calcium which is not a trace metal is related to the trace metals in a very important and special way. The absorption of trace metals by living things from the environment is inversely related to the concentration of environmental calcium (S-1). This means that the toxicity difference between hard and soft water can be very different (See Table I).

Table I (from S-1)

Metal	Ratio, toxic concentration in hard:soft water	Approximate toxicity in soft water (ppm)	Toxicity type (see text)
Titanium	14.6	8	II, III
Vanadium	4.2-9.2	5	I
Chromium	15	5	I, II
Iron	77	1.3	I, II
Nickel	24	4	I, II
Copper	15-500	<0.1	I, II
Zinc	3-67	2	I, II
Arsenic	--	--	II, III
Zirconium	8.2	14	??
Cadmium	5.5	<0.1	III
Tin	±4	1	III
Lead	33	2	III

There are in general three types of toxicity as shown in Table I. The three types are; 1. deficiency - certain elements are necessary for existance of life even though the amounts needed are in the ppm (parts per million) or ppb (parts per billion) ranges, 2. excess - given large enough amounts of any element it is toxic, and 3. disorders - caused by metals for which there are poor homeostatic mechanisms and which accumulate in man with age.

A somewhat oversimplified way (P-2) of looking at the relative effects of essential and non-essential trace elements is shown in Fig. 1. The horizontal scale is the logarithm of ppm of the element in the environment and the verticle scale goes roughly from life at the bottom to death at the top. Normal represents the amounts giving rise to healthy life and anything above this is detrimental to life. As can be seen, too much of a non-essential element or too little of an essential element can be fatal. In general if a non-essential element is present in the human environment (water, air, or food) in excess of a few ppm it can cause deliterious effects.

The body can with varying degrees of efficiency eliminate excess amounts of unnecessary elements. Most metals with the exception of cadmium and strontium are excreted by the intestines. Cadmium and strontium are eliminated by the kidney (S-1). The body alters the valence of a soluble metal to that required during or after absorption from the intestine. This phenomenon has been demonstrated for manganese, iron, cobalt and copper and partly for chromium (S-1). This fact shows that the determination of the charge state of trace elements in water supplies, food and humans is important to measure.

Interactions between trace metals complicate toxicological and health studies. For example, a zinc deficiency causes severe anemia in rats, rabbits and pigs which is indistinguishable from iron deficiency anemia, even when there is abundant iron in the tissues (D-1).

In another example "teart" in field animals is apparently due to high levels of molybdenum in the pasture and is controlled by administering copper salts to the animal suffering from the condition (D-1).

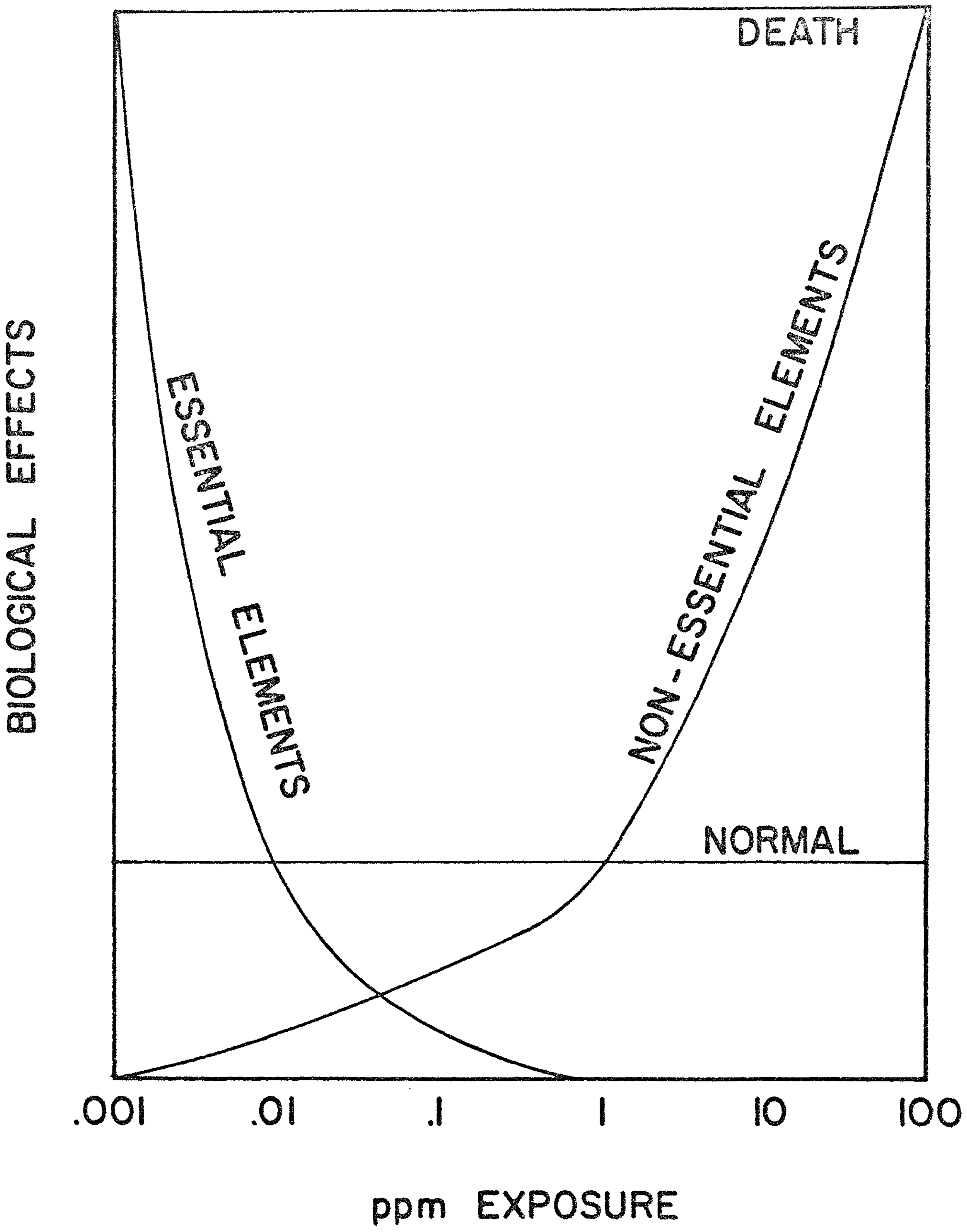


Figure 1 Simplified representation of the health effects of trace elements.

B. Specific Health Effects of Trace Metals

Little is known about the effects of ppm metals in animals and the essentiality of several metals found in mammals is questionable. Some insight into the problem can be learned from studying the toxic and health effects of trace metals in animals. The following discussion covers most of the metals found in this work and suggests that more toxicological and health effect studies are required in many of these areas.

Titanium

Tetravalent titanium when added to the drinking water in a concentration of 5 ppm increased the growth of mice but did not significantly affect mortality (S-2). Christie et al (C-1) found no evidence of pulmonary effects when rats inhaled titanium dioxide. Titanium accumulates with age in man, but there is no evidence that it is an essential metal (S-2). Thus it appears that in ppm and smaller amounts, titanium is not a serious health hazard.

Vanadium

There is no known reason why vanadium is essential to man (S-4). It is not a toxic trace metal for man but in large doses (of about 160 ppm) it will kill a rat. No other trace metal has so long had so many supposed biological activities without having been proven to be essential.

Exposure to vanadium pentoxide dust produces a clinical syndrome characterized by irritation of the eyes, nose and throat followed by rales throughout the lungs and acute bronchospasm similar to bronchial asthma (Z-1). Vanadium pentoxide inhaled at the level of 100 ppm lowered the free cholesterol and phospholipid content of the liver in rabbits (M-1). It also has been found that vanadium enhanced the activity of monoamine oxidase, an enzyme which has been shown to be acutely anti-hypertensive in rats and dogs and which inactivates angiotensin (P-1).

Vanadium has been found to inhibit the synthesis of cholesterol in rat liver cells (S-3 & A-1). However, most of the ingested vanadium is excreted within 24 hours (C-2).

Congestion and fine droplets of fat in the liver have been produced by the administration of vanadium compounds to rats. Reduction in fat and lipid content of adrenal cortex occured at the same time (M-1). Additional microgram quantities of vanadium acetate or metavanadate to minced liver slices caused increased oxygen uptake.

In man, intramuscular injection of sodium tetravaradate resulted in increased catabolism as indicated by increased output of all nitrogen, sulfur and phosphorous constituents determined in the urine (M-1). Ingestion of vanadium pentoxide at dietary levels beginning at 100 ppm vanadium caused lessening of custine content of rat hair (M-1). Thus it appears that the presence of vanadium at the ppm level is not a health hazard to man.

Chromium

Hexavalent chromium has been considered a toxic metal for many years. Trivalent chromium is less toxic although it raises the glucose tolerance of rats and rabbits (S-5). However it is not clear whether either is an essential element for man. Schroeder et. al (S-5) feels that chromium has not been definitely proven to be a carcinogen. The toxicity of fish to hexavalent chromium is fairly high in that 1.2-5.0 ppm is fatal to many species (S-5).

Considerable evidence does exist to show that chromium in the atmosphere inhaled by man can be a carcinogen. Hill and Warden (H-2) suggest that chromyl chloride may play an important role in the formation of lung cancer in chromate workers. Hueper (H-1) pointed out that the existance of a serious lung cancer hazard for producers of chromates from chromite ore and tar handlers of certain chromium pigments (zinc chromate, barium chromate and lead chromate) is well documented among workers in these plants.

Hueper also reported that the development of squanamous cell carcinomas of the lung and sarcomas of the lung and of the soft tissues of the thigh of rats which had received intrapleural or intramuscular implants of powered chromite ore roast suspended in sheep fat. Shelley (S-6) has pointed out that chromium in welding fumes was the cause of exzematous eruptions of the palms of the workers.

Calcium chromate, sintered calcium chromate and sintered chromium trioxide when introduced in pellet form into the pleural cavity of rats produce cancers, mainly sarcomas, in the majority of animals at the site of implantation within 14 months (H-1). This effect is related to the solubility of these compounds in the watery medium. It has been reported that as little as 0.7 ppm of chromium in the water can be toxic to some aquatic insects.

Thus it can be concluded that chromium may not be an essential element to man, that it may be a carcinogen and that hexovalent chromium is toxic to man at fairly low levels.

Iron

Iron has long been known as an essential element because of its importance in the hemoglobin of blood. Iron is not considered as a pulmonary irritant (K-1 & A-2) although Bonser et al (B-1) claim industrial proof of iron causing lung cancer. It almost seems that at some time, someone has shown everything to be a carcinogen--iron seems to be the least likely carcinogen among the trace metals.

Nickel

Nickel is one of the relatively non-toxic metals found in the tissues of man, ranking in this respect with the essential elements, iron, cobalt, copper anc zinc. Its physiological role, if any, has not been established. The toxicity for mammals is low, ranking with the essential metals and with chromium, barium and silver (S-7).

Nickel carbonyl vapors have been shown to cause pulmonary cancer (S-8), acute pheumonitis (S-9), alterations in ribonucleic acid (S-10) and appears to be related to acute mycardial infarction (S-11). Nickel dust has shown a correlation with lung cancer (M-2) and inhalation of powdered metallic nickel (15 mg/m^3 in air) has been shown to cause pulmonary lesions in guinea pigs and rats (H-4). Nickel carbonyl is highly toxic by inhalation. The LD_{50} values (the amount that kills 50% of the animals) for 30 minute exposure for mice, rats, and cats are 10, 35, and 270 ppm by volume, respectively. It is suspected of causing a high incidence of carcinoma of the respiratory passages after long exposure to low concentrations (K-2).

Little seems to be published concerning the effects of nickel in water supplies, although 6 ppm appears to be toxic for some aquatic insects and the lethal dose for fish is in the range of 0.08-1.0 ppm (W-1).

Copper

Forage with too much copper can cause fatal hemolytic anemia and hepatic necrosis in cattle and sheep. Copper toxicity is a fundamental cause of Wilson's disease (S-12). Recognition of the facts that this disorder is inherited as an autosomal recessive trait and is the only example of significant copper toxicity in man. This has made clear that man has had to develop a mechanism, transmitted from one generation to the next which prevents copper poisoning in all the rest of us.

The geographic location has influence on the biological priorities related to copper intake. In Florida cattle with 60 ppm Cu on dry weight basis were often showing severe diarrhea, achromotrichia, bone change, and anemia and severe reproductive disturbances. Yet in the Netherlands and in Oregon values of 25 ppm Cu are found in the liver with the animals apparently in normal health (D-1).

Although not much information appears to be available concerning the effects of copper in water supplies, it is known that 0.01-1.7 ppm Cu is the toxic range for fish and as little as 0.027 ppm Cu can be toxic to aquatic insects (W-1).

Zinc

It has long been known that zinc deficiency had an adverse effect on human health (S-13). For example, it leads to subnormal growth and impairment of intestinal absorption. Protein and RNA are markedly affected by zinc deprivation. The normal intake of zinc in the diet is 90 mg of zinc for one kg of the animal. When this intake is reduced to 12 mg/kg, serious effects are exhibited by protein and RNA (0-1). However, excess amounts of zinc (in the 0.5% to 1.0% range of zinc oxide) also affect growth rate and decrease both the weight and fat content of the liver (this was observed on a high fat-low protein diet). It also interferes with the development and mineralization of bones. Zinc at these same levels affects metabolism to a considerable extent. It causes increased excretion of nitrogen suggesting a general wastage of tissue proteins and a decreased excretion of phosphorous and sulfur (S-13). This latter phenomenon is suggested as the mechanism for poor bone development and decreased liver weight. This intake of zinc oxide brings about a significant decrease in the phosphate activity of the intestine while increasing it in the liver and kidneys. Phosphate assimilation is known to be related directly to fat production.

Some information is available concerning the effects of atmospheric zinc on humans. Inhaled zinc in the form of zinc ammonium sulfate or zinc sulfate causes increased pulmonary flow resistance (F-1).

Adding a supplement of zinc (0.25%-0.75%) for a few weeks to the diet produced a decrease in the normal deposition of calcium and phosphorous in the bones of young rats which was alleviated with calcium and phosphorous supplements. However, the calcium and phosphorous supplements prevented the accumulation of zinc in the bone. These levels of zinc have an adverse effect on both the absorption and utilization of magnesium (S-14).

Excess dietary zinc causes a hypochromic, microcytic anemia in rats (G-1). This anemia is wholly or partially alleviated by feeding additional copper. This suggests that excess zinc causes decreased copper resulting in anemia by affecting hemoglobin formation (at levels of zinc in the 1.0% to 1.5% range) (D-2). The 1.0% zinc reduced hemoglobin concentration by 40% and 0.03% copper restored the hemoglobin level. Excess dietary zinc also causes a lowering of the enzyme activity of cytochrome oxidase. Adding copper increased this enzyme activity.

As little as 0.3 ppm of zinc is toxic to some aquatic insects and 0.3-0.7 ppm is the toxicity range for fish. Thus it can be concluded that zinc is an essential element, but in fairly low concentrations it is a trace metal which can cause serious effects not only in fish and insects but also in mammals.

Arsenic

In general, the most stable natural valence of an element, that normally found in soil and water, is the least toxic, for example chromium (III), manganese (II) and arsenic (V) as opposed to the very toxic chromium (VI), manganese (VII) and arsenic (III). Sodium arsenate is non-toxic in amounts 100 times as large as the LD (lethal dose) of trivalent arsenic. Commercial arsenic is almost entirely the trivalent oxide (S-17).

Adding 12-15 ppm of arsenate counteracts selenium poisoning in cattle, dogs and chickens. Metallic arsenates, potassium calcium and lead are toxic to insects (S-17). However, Warnick and Bell (W-1) say that less than 20 ppm of arsenic is not toxic to aquatic insects.

Industrial exposures of arsenic can give rise to keratosis of the skin that occasionally become malignant. However, most attempts to produce cancer with arsenic have been unsuccessful (S-17). Arsenite given in a dose of 5 micrograms per milliliter of water significantly decreased the incidence of all tumors, except malignant ones where no effect was noted (K-3). Intravenous injection of 20 mg/kg of sodium arsenate in pregnant golden hamsters led to a high incidence of malformations of the embryos (F-2). Buechley (B-2) made the suggestion that the epidemiological chain for cancer leads from arsenic high mines and smelters, through arsenical insecticides to arsenic-sprayed tobaccos used in cigarettes. Along this line, lung cancer appears to be proportional to the amount of inhaled arsenic.

If arsenic is an essential trace element for mammals, the requirements are of the order of one microgram per day or less (A-17).

Trivalent arsenic given at a dose of 5 ppm in drinking water for the life of a mouse showed a slight tendency to accumulate in the heart and lung and was slightly toxic in terms of medium life span, longevity and survival, but not in terms of growth (S-15). Arsenic trioxide fed in drinking water in concentration of 0.01% reduced the number of induced cutaneous malignant skin tumors. It is still questionable whether arsenic is carcinogenic (M-3). Arsenite given in 5 ppm in drinking water caused the accumulation of arsenic in the aorta and red blood cells with no signs of toxicity (S-16).

Chronic arsenic intoxication by ingestion is usually characterized by weakness, loss of appetite, gastrointestinal disturbances, peripheral neuritis, occasionally hepatitis and skin disorders such as keratosis and pigmentation (H-4). The common gray form of elemental arsenic is essentially non poisonous by ingestion and most of it is eliminated unchanged. The oral LD of arsenic trioxide in man is between 70 and 180 mg/kg. Thus although arsenic is not a serious health problem at the ppm level, it is an undesirable trace metal in water supplies.

Zirconium

Compounds of zirconium have a low order of toxicity to animals. The only recorded effect of toxicity of zirconium to human beings involves cutaneous exposure from deodorant sticks and poison-oak lotions (S-19). When mice were fed 5 ppm in their drinking water (S-18 & K-4) it was found that no carcinogenic or tumorigenic effects were produced. The mice did show a slightly shortened life span (about one month in 30 months).

Animals do absorb some zirconium if it is broken down enough to pass through membrane walls. There is no good analytical evidence that zirconium is consistently absorbed in rats. Also no evidence exists that zirconium as fed to rats through their drinking water has any biological activity except possibly to effect weight of older animals (S-20). Schroeder and Balassa (S-19) suggest that zirconium is an abnormal (non-essential) element in man.

Cadmium

Cadmium, usually considered a toxic metal, and under certain circumstances a nephrotoxic one, has been found in the kidneys of all adult human beings from many cities of the world. It is virtually absent in newborns and accumulates with age. There is no known biological function for cadmium in man (S-23).

A marked correlation (r = 0.76) exists between the concentration of cadmium in the air and death rates from hypertension and arteriosclerotic heart diseases (C-3). Zinc showed a similar correlation with r = 0.56.

Feeding the environmental toxicant cadmium (75 mg/kg) to young Japanese quail for four weeks produced growth retardation, severe anemia, low concentrations of iron in the liver and high concentrations of cadmium in the liver. Dietary ascorbic acid supplements (0.5 and 1.0% by weight) almost completely prevented the anemia and improved the growth rate but did not markedly alter concentrations of iron or cadmium in the liver (F-3). It has been found that 0.1 ppm of cadmium is toxic to some aquatic insects and 0.01 -10 ppm is toxic to fish (W-1).

Cadmium in concentrations of 5 ppm were given via their drinking water to mice. This level showed an innate toxicity in terms of survival of male mice (S-2). Hypertension was induced in rats by adding 5 ppm cadmium to their drinking water. Females were more susceptible at all ages. Cadmium was found in the livers and kidneys of all rats. Along with the hypertension in older rats went salt (sodium cloride) hunger (S-24 & S-21). Rats fed 10 ppm of cadmium in water showed in 2-4 months chronic arterial hypertension (S-22). Thus cadmium is a serious health hazard in water supplies in the ppm range.

Tin

Feeding 5 ppm tin in drinking water to mice produced no increase or decrease in tumor formation (S-15). Tin is not known to be toxic to mice or to affect their growth rate (K-3).

III. X-Ray Fluorescence

A. Introduction

That X-rays might be used in analytical techniques for the identification of elements was first discussed by Moseley (M-4) in 1913. He determined that the X-rays given off from the target material in an X-ray tube were composed of several wavelengths known as the K and L series. He also showed that the wavelengths of each series were directly related to the atomic number of the element, the square root of the frequency increasing by an equal amount for each change of atomic number. The first general work that appeared concerning X-ray emission spectrography was Von Hevesy's "Chemical Analysis by X-rays and its Applications" which appeared in 1932 (H-5). During the following decade, X-ray emission spectrography began to be used for chemical analysis, usually when the spectra from emission spectrographs were too complex to analyze. However, for a number of reasons, X-ray emission spectrography was not widely used; viz., X-rays were known to be hazardous, but these hazards were not well understood (as many of those who lost parts of their bodies can well testify), the apparatus was quite costly, the sample had to be somehow attached to the target in the tube and the heat generated there often destroyed the sample, the efficiency for excitation was very small compared to the broad background produced from the target and the analysis equipment was far from being very sensitive. Almost all analysis during this period were qualitative. One of the largest achievements of X-ray emission spectrography during this period was the discovery of Hafnium by Von Hevesy and Coster by measurement of its X-ray emission spectrum (H-6).

The above method creates X-rays by electron bombardment in the X-ray tube itself. Some of the problems inherent in this approach can be eliminated by a modification. The X-rays produced by the X-ray tube can be used to excite the atoms whose characteristic X-ray energies are lower in energy than the energy of the exciting radiation. This process is similar to optical fluorescence and the X-rays produced are identical to those produced by electron bombardment. This secondary process is called X-ray fluorescence (XRF). X-ray fluorescence is superior to the earlier technique of X-ray emission in identifying elements because the background continuum is considerably reduced. In fact the background in XRF is due only to the backing material and the thickness of the sample. Thus it is important to prepare samples which are as thin as possible and whose backing material is as thin as possible.

Prior to 1945, XRF was not very widely used because it required a very high power X-ray tube and the analyzing techniques were not reliable enough. These techniques involved using a photographic plate or geiger tube to record the X-ray output as a function of the Bragg angle of the analyzing crystal. After 1945, instrumentation became available which made XRF practical. In 1948 Friedman and Birks (F-4) described a plane crystal X-ray spectrograph suitable for routine use. By 1954 the General Electric Company had produced a focusing spectrograph with a bent mica crystal for use in XRF (A-3 & P-3). However, it was not until 1956 through the efforts of the Dutch Phillips Company that XRF began to be used routinely in analytical laboratories (J-2). In general, these devices were costly, bulky and by no means portable.

Two recent developments have greatly simplified XRF and may eventually lead to reasonable low cost instruments which are portable. The first development occured shortly after World War II. The existance of large nuclear reactors made possible the fabrication of very intense radioactive sources which could be used to excite the X-ray fluorescence in place of the bulky X-ray tubes. At present, sources as large as 25 mc are commercially available which are the size of a pin head (A-7) and are relatively inexpensive (lower in cost than X-ray tubes). Although artificially produced radioactive sources have been available for several years they were not extensively used in XRF until a second new development.

In 1964, solid state detectors were developed by drifting lithium into germanium and silicon which revolutionized the spectrographic measurements of gamma rays and X-rays (E-1, G-2, & E-2). These detectors were capable of resolutions roughly an order of magnitude better than the best of the previous detectors, namely the scintillation detectors (such as NaI and CsI). This development provided for the first time a multichannel detector capable of resolving X-rays for a large number of elements (B-3). The earliest detectors had resolutions at the iron K X-ray line (6.4 keV) of about 1000 eV. However, at the present time detectors are commercially available with resolutions of 170 eV at the iron line. Fig. 2 shows how these resolutions compare to the separation energy of X-rays as a function of Z. As can be seen from this figure, these detectors are capable of resolving all X-rays of interest. The one disadvantage of these detectors is that to achieve the ultimate resolution (which is necessary in XRF work) they have to be cooled to liquid nitrogen temperatures (77°K). This requires a large reservoir of liquid nitrogen to be part of the unit. The size of the detectors is quite small (they typically have surface areas of 50-80 mm^2 and depths of 3 mm) so if one can be developed which does not need to be cooled, the entire apparatus of XRF could be made portable. Portable equipment involving the XRF technique has already been developed for determination of the presence of only one element (L-2). The addition of

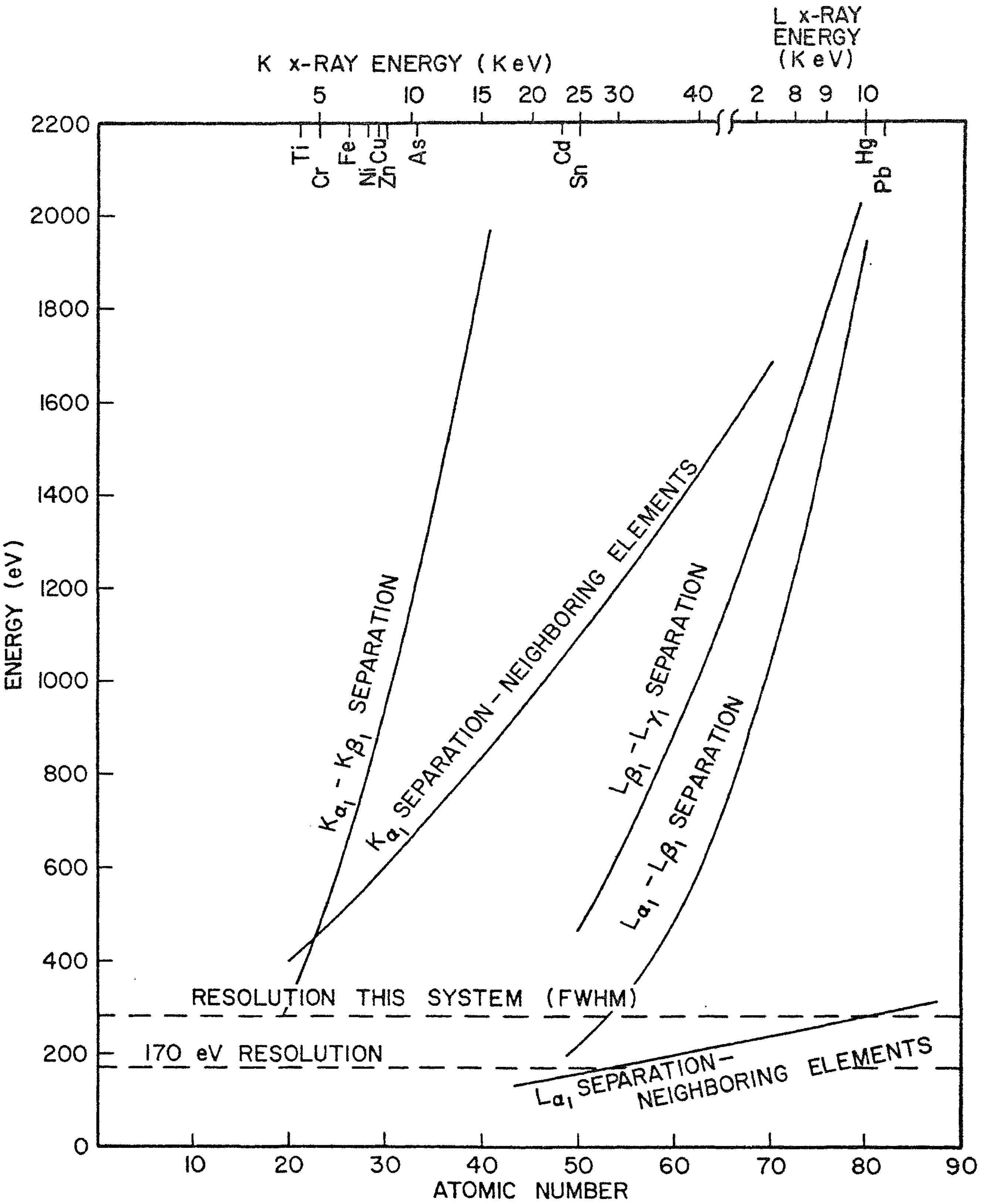


Figure 2. A comparison between the resolution of solid state detectors and separation energies of X-rays.

solid state detectors to these devices will allow all metals to be detected simultaneously. Recent work has been conducted to develop room temperature detectors (M-5) with CdTe and other II-VI compounds which shows promise. The major problem in this work is in developing high purity crystals.

B. Principles of X-ray Fluorescence Spectrography

Consider a beam of electromagnetic radiation (gamma rays, X-rays, bremstrahlung, or even electrons) impinging on an atom and penetrating the outer orbits. If the beam has sufficient energy, it may displace an electron from the closest shell to the nucleus, the K shell. Simultaneously there will be a sudden absorption of energy from the beam and a corresponding increase in the mass absorption coefficient as shown in figures 3 and 4 (G-3). The positions of these sudden increases are called absorption edges. To occupy the resulting hole in the K shell, an electron will fall from a higher orbit, usually the L or M shell. As a result of this transition, energy will be released in the form of an X-ray, whose magnitude depends on the atomic number of the atom and the orbit from which the electron falls. If an electron falls from the L shell to the K shell, it gives rise to a K line. There are actually three sub-orbits in the L shell but transitions from one of them is quantum mechanically forbidden. The X-rays resulting from the transitions from the other two levels are called the $K_{\alpha 1}$ and the $K_{\alpha 2}$ lines, the former being from the higher lying L shell. Electrons can fall from the M shells and even though there are five M sub-shells, only two X-rays are possible, these are labeled $K_{\beta 1}$ and $K_{\beta 2}$. In a similar way, electrons removed from the L orbits will be replaced by electrons from the M orbits, giving rise to the L spectrum, of which the analytically significant lines are $L_{\alpha 1}$, $L_{\alpha 2}$, $L_{\beta 1}$, $L_{\beta 2}$ and sometimes $L_{\gamma 1}$ (W-2).

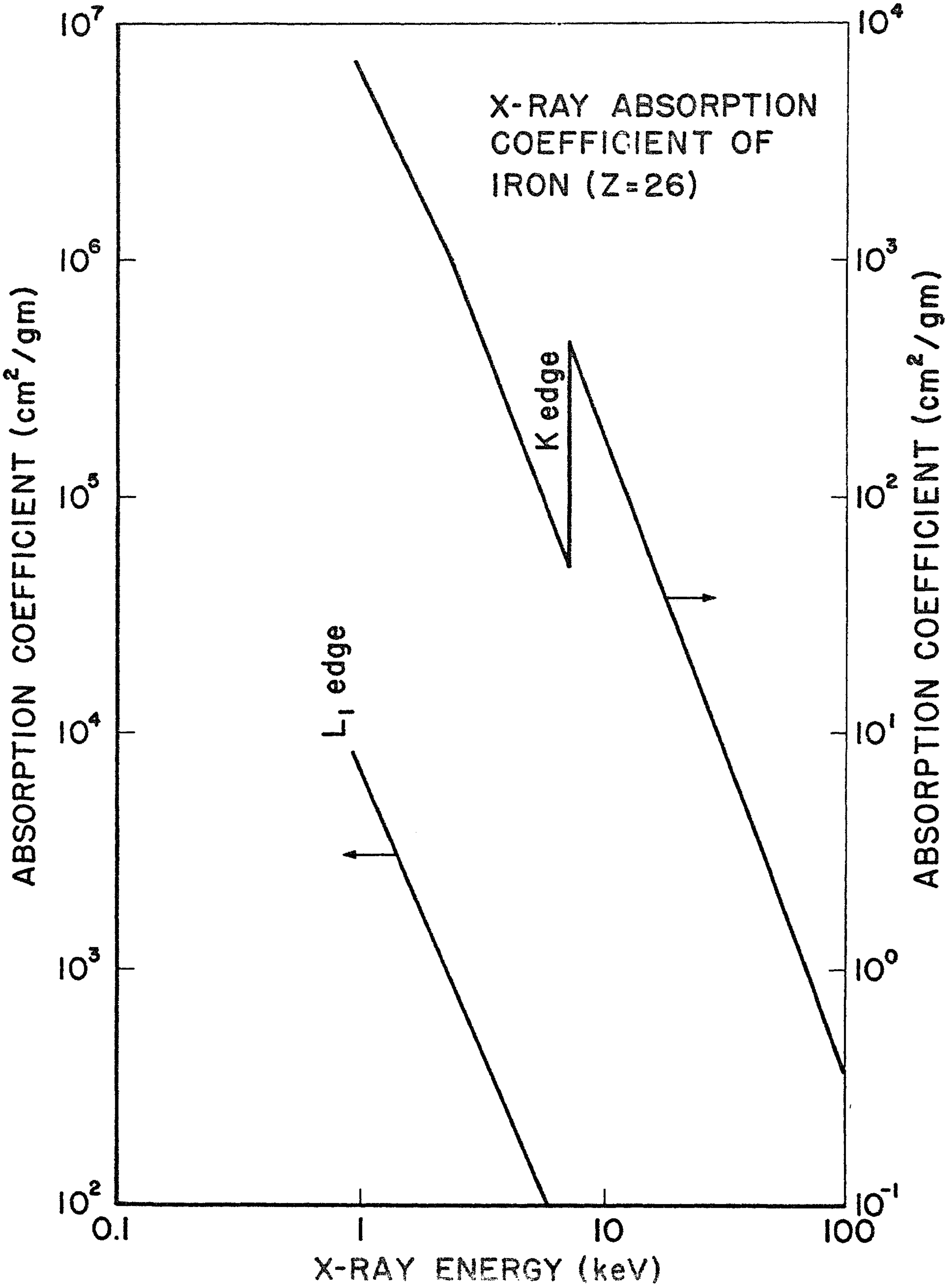


Figure 3. X-ray absorption coefficient of iron as a function of energy (G-3).

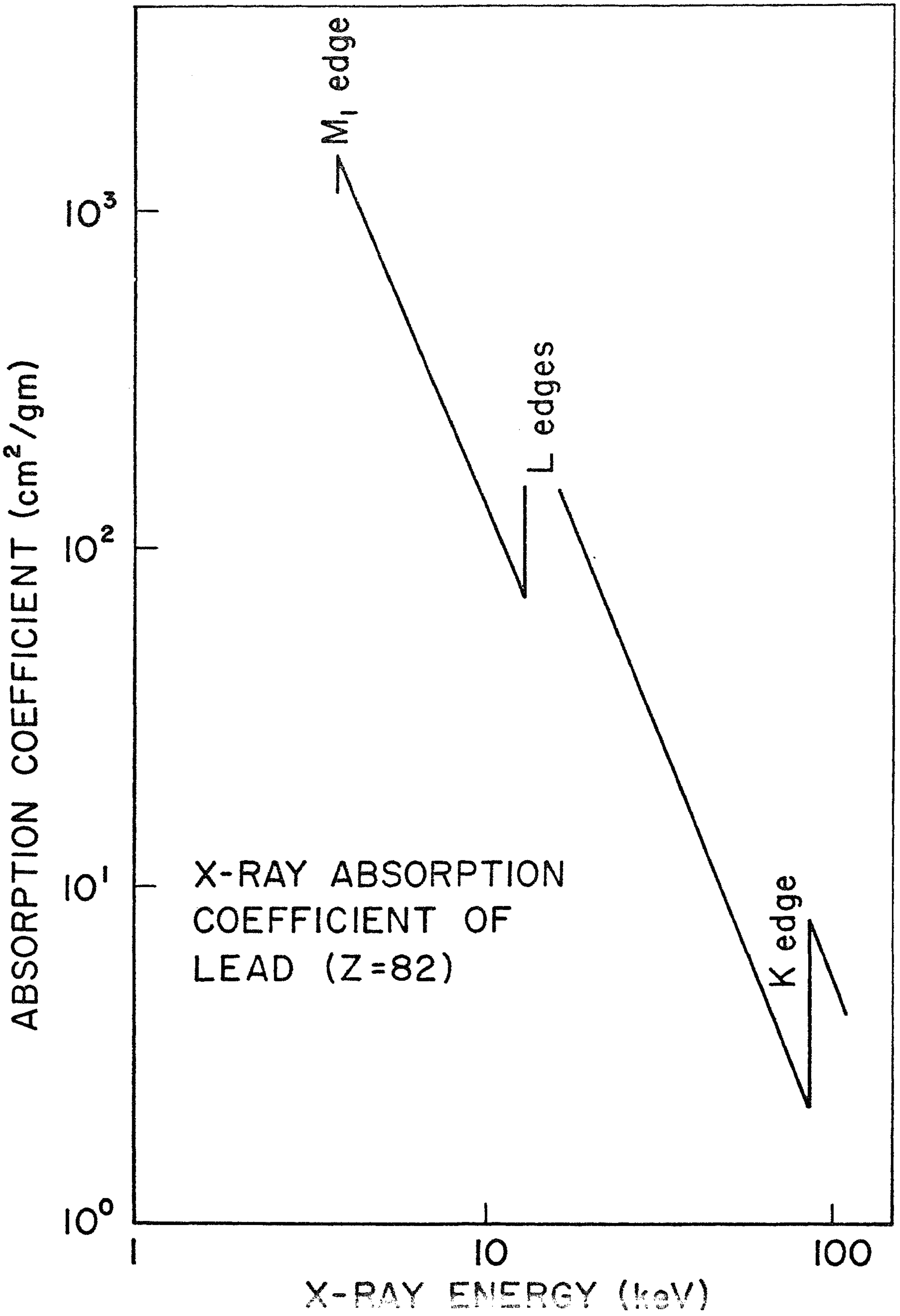


Figure 4. X-ray absorption coefficient of lead as a function of energy (G-3).

TABLE II

Z	ELEMENT	Kα1	Kβ1	Lα1	Lβ1
22	titanium	4.511	4.932	-	-
23	vanadium	4.952	5.427		
26	iron	6.404	7.058	-	-
28	nickel	7.478	8.265	-	-
29	copper	8.048	8.905	-	-
30	zinc	8.639	9.572	-	-
48	cadmium	23.174	26.095	-	-
50	tin	25.271	28.486	-	-
82	lead	74.969	84.936	10.551	12.614

Table III

Kα1	1	Lα1	1
Kα2	1/2	Lα2	1/2
Kβ1	1/5	Lβ1	1/5
Kβ2	1/33	Lβ2	1/10
		Lγ1	1/10
		Lβ3	1/15
		Lβ4	1/25

x = sample thickness

E = enhancement factor.

The two geometrical factors in the above equation can be maximized by placing the exciting source, sample and detector as close as possible. These factors can also be increased by using a detector of large surface area. Detectors with active areas as large as 500 mm^2 are now commercially available (O-2 & K-7). The main contribution to the smallness of the geometrical factors is the necessity to shield the detector from the exciting source. The fluorescence yield, ω_k, depends solely upon the element being considered (F-5) and cannot be improved by experimental conditions.

The intrinsic detector efficiency, ϵ_D, of lithium drifted silicon solid state detectors is quite high and is one of the very desirable features of these detectors. Fig. 5 shows this efficiency as a function of energy (O-2). For the range of energies between roughly 10 and 20 keV, the efficiency is almost 100%.

The factor, k_{abs}, is a function of the probability of K-shell absorption (as opposed to absorption by another electronic shell), photoelectric absorption coefficient, and sample thickness. The probability of K-shell absorption is a function of Z and the energy of the excitation source. This probability is 80% or better for most of the metals of interest in this report. The photoelectric absorption coefficient is also a function of Z and the excitation energy. The factor k_{abs} can be maximized by choosing an excitation energy as close as possible to being just above the characteristic X-ray energy of the element of interest. However, background due to backscatter will increase greatly under these conditions (Y-2).

The overall count rate can also be increased by increasing the intensity of the excitation source. However, as the source strength is increasing, so

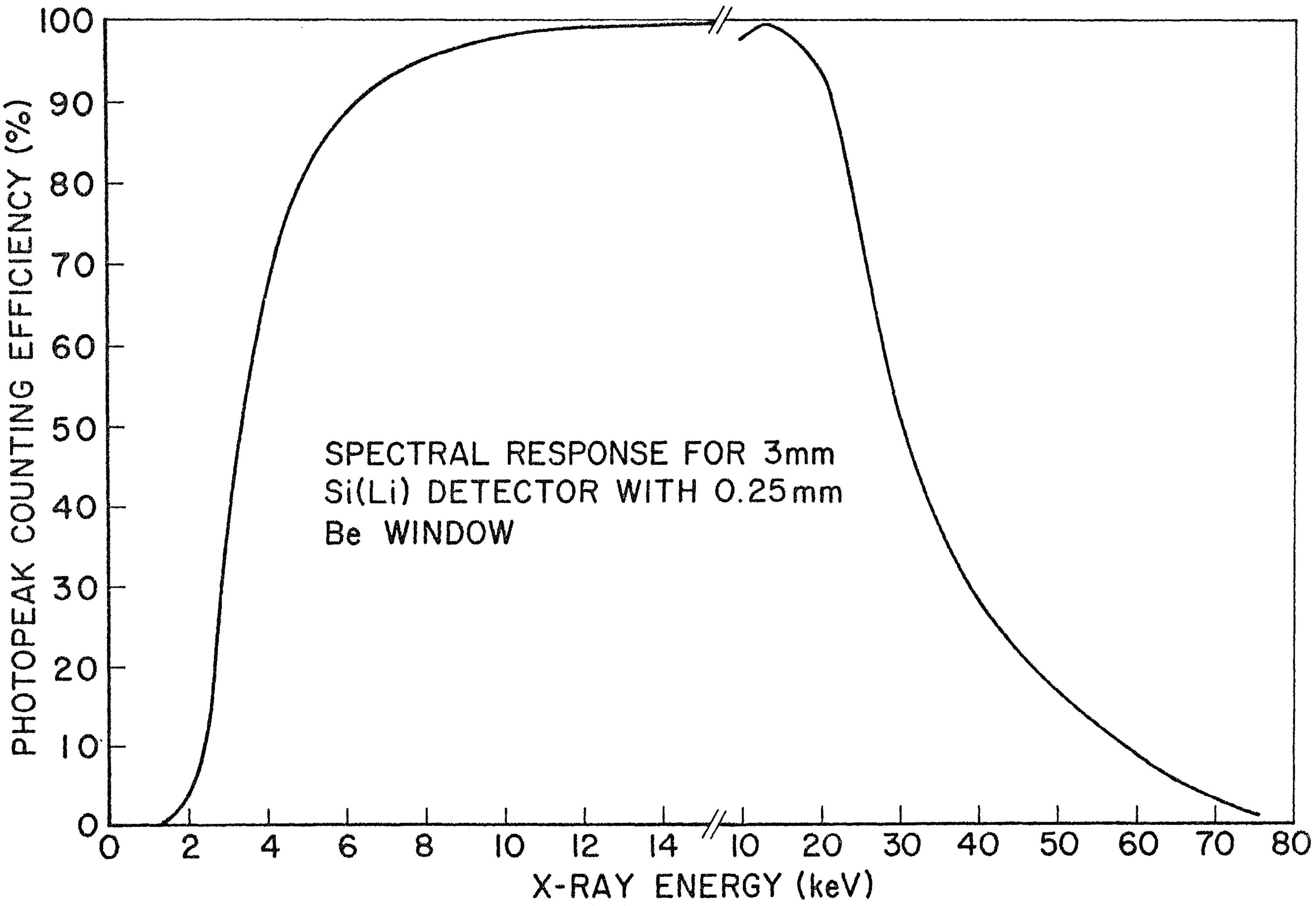


Figure 5. Efficiency curve for the Si(Li) detector used in the present work.

is the backscatter contribution to the background. But since the detection limit is inversely proportional to $S/\sqrt{B}$, where S is the signal strength and B is the background, over all count rate can be increased by increasing S (Z-2).

The most important factor which limits the sensitivity of XRF is the number of background counts. Essentially the standard deviation of the background ($\sqrt{B}$) is the limit of detection ability of trace elements (the accepted criterion is to use $3\sqrt{B}$ as the sensitivity limit). The level of the background depends on other elements in the sample besides those being fluoresced, the sample backing and any other materials in the vacinity of the detector including the sample holder and table on which the apparatus is sitting, and even the air itself. For this last reason, when analyzing for very low Z elements it is advisable to place the source, sample and detector system in a vacuum system. At very low count rates, the electronic noise will also contribute to the background level.

In some cases it is necessary to concentrate a water sample or otherwise chemically treat it to remove interfering elements (L-1 & H-8). However, such a procedure will change the chemical makeup of the sample and possibly introduce trace elements from the chemicals used. Performing chemistry on the samples eliminates the desirable non-destructive feature of XRF and because of this and the above reasons it is not a desirable procedure, and usually not a necessary one.

Elements of low Z such as Na, F, O, B, Be and Li cannot be detected by normal procedures with XRF because of the difficulty of detecting their respective low energy X-rays. However, by using a stoichiometric compound of a light element and a heavy element Luke (L-3) has been able to determine the presence of the light element indirectly by measuring the amount of the heavy element present. Recently, techniques have been developed to analyze liquid samples with XRF (S-31).

Recently a number of workers (B-4, J-1, K-8 and C-4) have shown that considerably higher exciting efficiencies can be obtained by using charged particles from nuclear accelerators rather than radioactive sources to produce the X-ray fluorescence. In general, protons and alpha particles with energies of a few MeV and oxygen ions of 15 MeV have been used achieving sensitivities in the 10^{-12} range. The increased sensitivity of this technique is due to the high crossections for the charged particle production of X-rays (G-6). The best sensitivity for proton induced XRF is the range 10-20 MeV (D-3).

More details concerning the principles and techniques of XRF may be found in references K-6 and A-4.

C. Apparatus for X-ray Fluorescence Analysis

Probably the most important single part of the equipment for XRF is the solid state Si(Li) detector. The detector used in this study had an active area of 80 mm^2 and a depth of 3 mm. Its operating voltage was 1000V. Since the detector was cooled to 77°K by liquid nitrogen, it was enclosed in a vacuum cryostat to eliminate condensation (see Fig. 6). The beryllium window on the front of the cryostat was 0.25 mm thick and the gold dead layer on the front of the detector was 100-200 A° thick (O-2). An incident radiation penetrates this dead layer and creates electron-hole pairs (one pair per 2.9 eV) in the charge-free active area (A) or depletion region. These pairs are then "swept" away (the arrow in Fig. 7 indicates the direction) by means of the potential difference obtained through the applied bias voltage; hence, an amount of charge that is proportional to the energy deposited in the crystal is received at the positive bias lead.

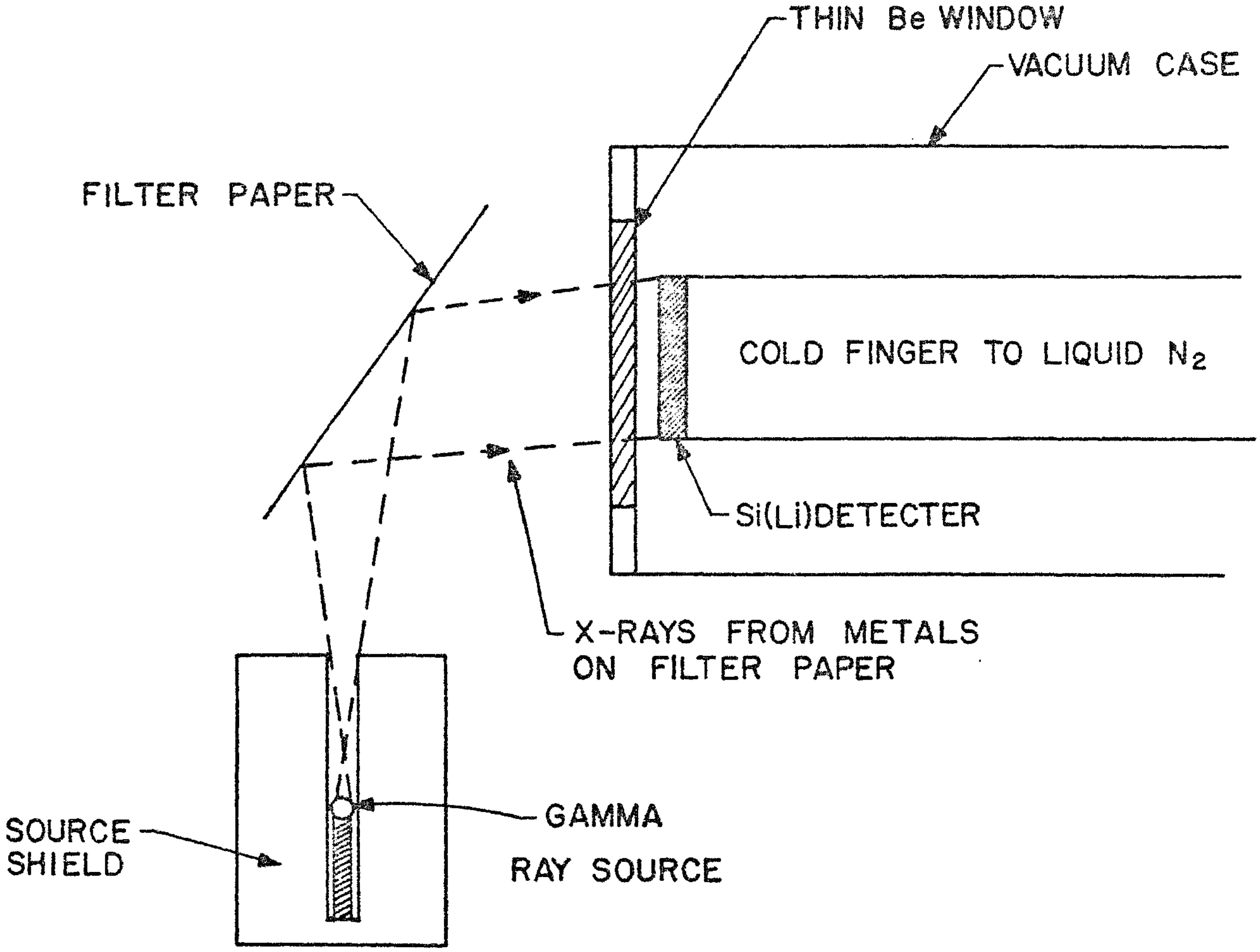


Figure 6. Geometrical arrangement of exciting source, sample and detector.

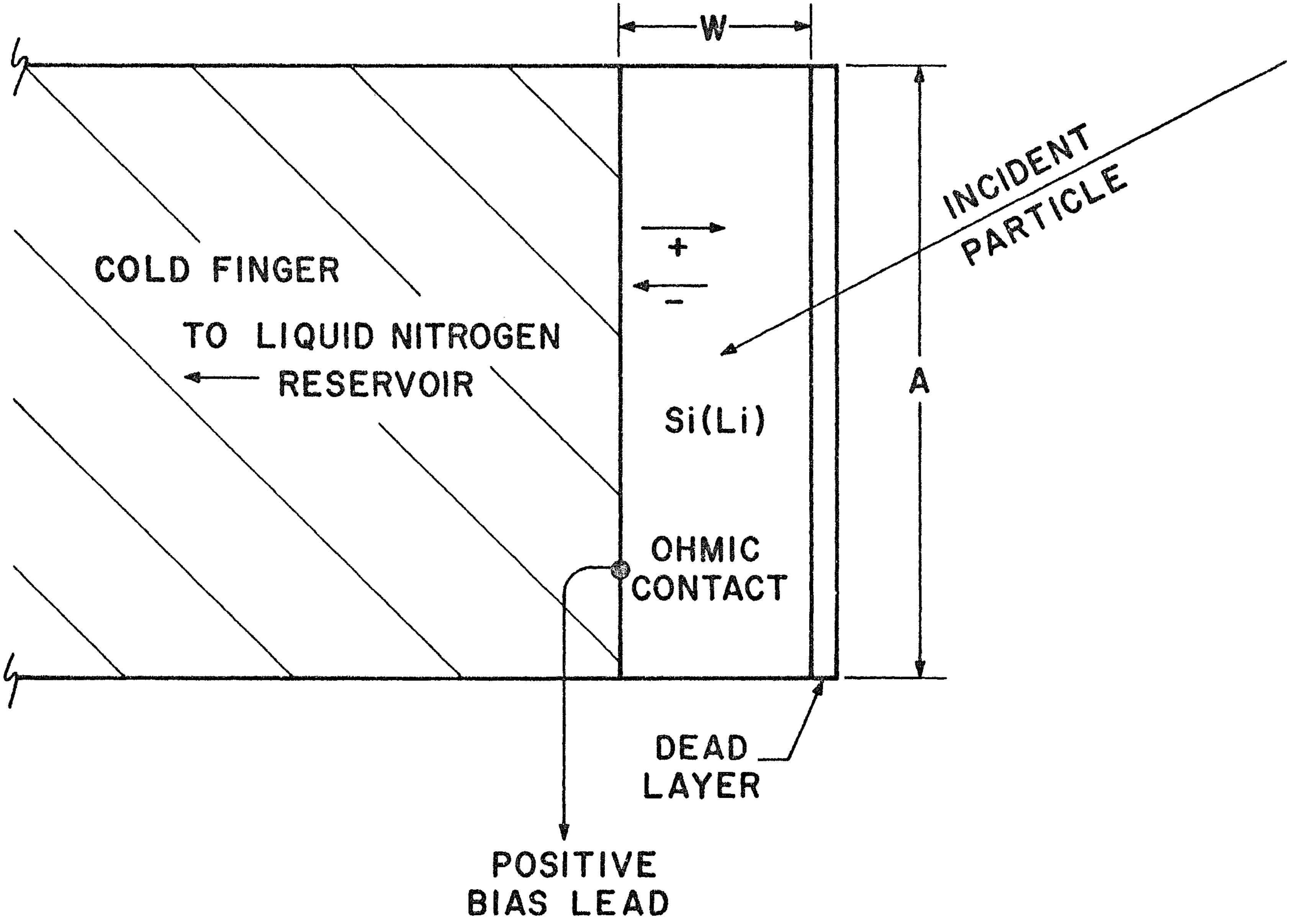


Figure 7. Schematic drawing of a lithium drifted silicon detector.

The important characteristics of the lithium drifted silicon detector for application in charged particle or electromagnetic radiation (such as X-rays) detection are:

a. the depletion depth (W);

b. the active area (A);

c. the purity of the active region;

d. the thickness of the dead layer.

Characteristics a and b determine the overall efficiency of the detector. Since the active area determines how many particles of the total number of disintegrations are obtained in the detector, and the depletion depth determines how many of these particles deposit their entire energy in the detector.

Characteristics c and d are important as far as energy resolution is concerned. The impurity of the depleted region governs the amount of free charge in this region. This free charge produces a reverse bias leakage current (or false signal--noise), which causes a broadening of spectral lines.

Except for minor effects at very low energies the number of electron-hole pairs created by an X-ray impinging on the detector is proportional to the energy of the X-ray. By connecting a charge sensitive preamplifier to this detector the accumulated charge collected by the bias voltage could be integrated resulting in a voltage pulse whose magnitude was proportional to the energy of the incoming X-ray and whose width in time is indicated by a rise time of a few microseconds. Commercially available systems include the detector, preamplifier and an amplifier capable of producing from the above described preamplifier, pulses in the 1-10 volt range with time widths of a few microseconds (O-2).

TABLE IV

Radioisotope	Half-life	Useful Radiations			Intensity per Disintegration (K-5)
Iron-55	2.6 years	5.90 keV	MnKα	X-ray	1.0
		6.49 keV	MnKβ	X-ray	0.2
Americium-241	458 years	13.9 keV	NpLα	X-ray	0.14
		17.8 keV	NpLβ	X-ray	0.18
		20.8 keV	NpLγ	X-ray	0.05
		26.4 keV		γ-ray	0.03
		59.6 keV		γ-ray	0.36
Cadmium-109	453 days	22.1 keV	AgKα	X-ray	0.7
		25.0 keV	AgKβ	X-ray	0.15
		87.7 keV		γ-ray	0.03
Iodine-125	60 days	27.4 keV	TeKα	X-ray	1.0
		31.0 keV	TeKβ	X-ray	0.2
		35.5 keV		γ-ray	0.07
Cobalt-57	270 days	14.4 keV		γ-ray	0.09
		122.0 keV		γ-ray	0.87
		136.3 keV		γ-ray	0.11
Promethium-147	2.7 years	See Fig. 8			

This brief introduction to lithium drifted silicon detector systems is assuredly limited only to the pertinent facts concerning their performance. For a more comprehensive treatment of the systems reference O-3 is an excellent introduction, while references G-4, M-5 and H-7 are more suitable for detailed considerations.

The voltage spectrum, which really is an energy spectrum, produced by the above system contains information concerning the energy of the X-rays present (qualitative analysis) and their relative intensities (quantitative analysis). These pulses are sorted according to voltage by a multichannel analyzer. This device divides the 10 volt range of the incoming pulses into 1024 channels and counts how many fall into each channel. The device used in the present work was manufactured by Northern Scientific, Ind. (N-1). If a complete analysis for all possible metals is desired, the multichannel analyzer will be the most expensive single component of the XRF system. If, however, only a few elements are important, this cost can be reduced considerably.

The system described above can be totally automated by adding an automatic sample changer and the need for human attention would be determined only by the number of samples that could be inserted in the changer (B-5 & B-6). The automation of the analysis of the data provided by the multichannel analyzer can be easily facilitated by using a computer. Because of the simplicity of the spectra, a computer program can be constructed which will print out information concerning which elements are present and their concentrations.

Table IV lists several of most useful radioisotopes which can be used to excite the X-rays. Note that the distinction in the description X-ray and gamma ray has nothing whatever to do with the characteristics of the photons, which are in fact identical, but only describes whether the photon originates from an atomic transition following nuclear capture of an orbital electron (X-ray) or whether the photon originates in a nuclear transition (gamma ray).

Because the fluorescent efficiency is highest when the exciting radiation is close in energy to that of the X-ray being produced, one would choose different of the above sources in Table IV for different elements. Promethium 147 was chosen for the present work because it produced a somewhat uniformly distributed energy spectrum and thus could excite a large number of elements with somewhat similar efficiencies (see Fig. 8). An Americium-241 exciting source was also used (Fig. 9) but its exciting efficiency was almost an order of magnitude less than the ^{147}Pm source. The source used in the present work (A-7) consisted of a ceramic bead approximately 2 mm in diameter which contained 1 curie of ^{147}Pm. This isotope decays by beta decay 100% to the ground state of ^{147}Sm. The accelerations of the electrons from the beta decay in the bead produce a bremstrahlung spectrum (S-26). The conversion efficiency of the bead used in this work was approximately 0.25%, which means that the effective strength of the exciting source was approximately 2.5 millicuries.

Consider now the situation where ^{125}I is being used to fluoresce a sample containing silver, zirconium, copper and iron. The radiations from the ^{125}I source are shown in Table IV and the absorption edges of these materials are 25.52, 18.00, 8.98 and 7.11 keV respectively. The resulting relative counting rate from these elements would be Ag:Zr:Cu:Fe 20:10:2:1. These ratios were calculated by assuming that the cross section for excitation goes roughly as the fifth power of the atomic number (S-25). If the element of interest is silver or zirconium, the count rates will be down considerably.

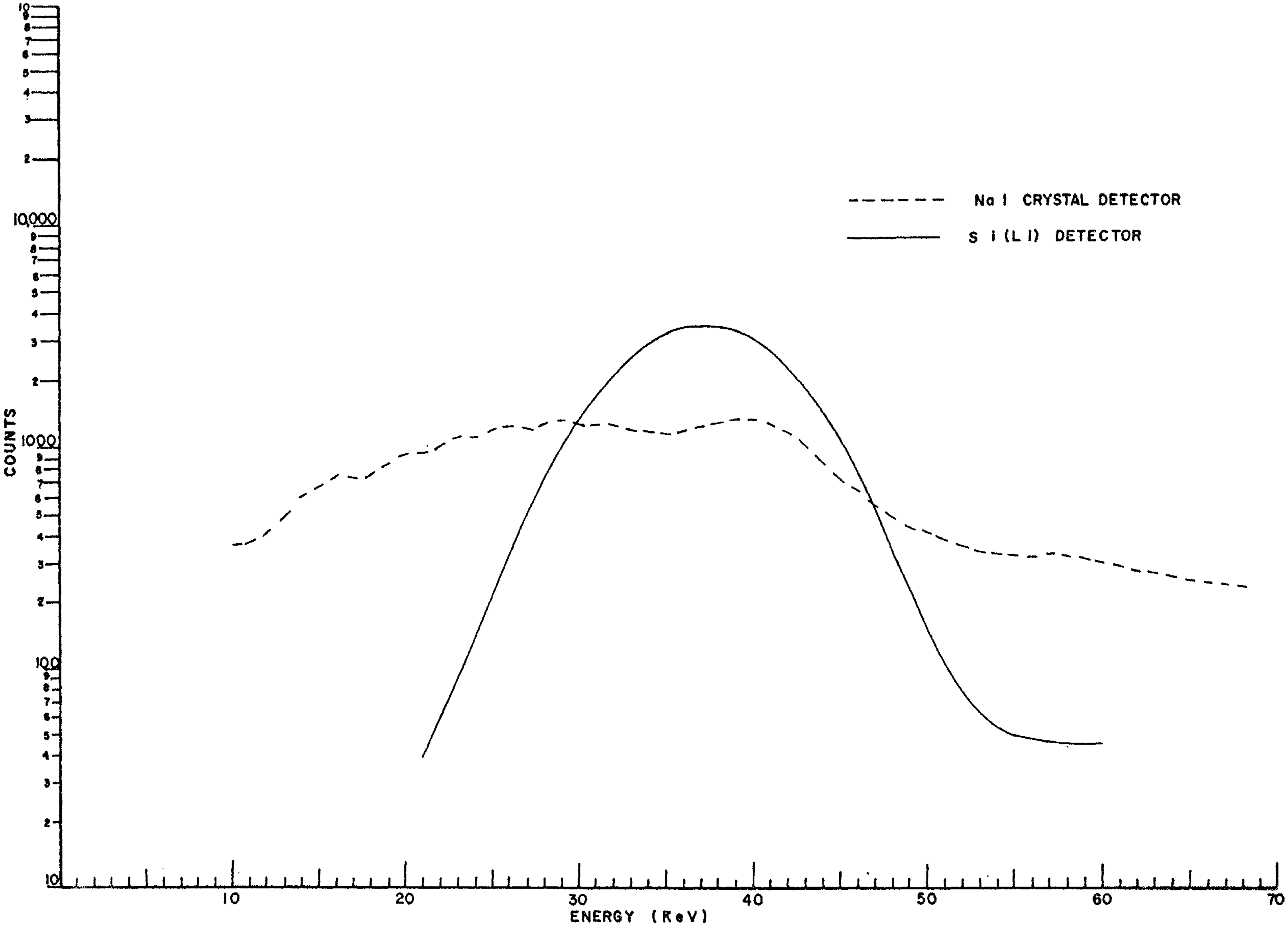


Figure 8. Bremsstrahlung energy spectrum produced by ^{147}Pm source.

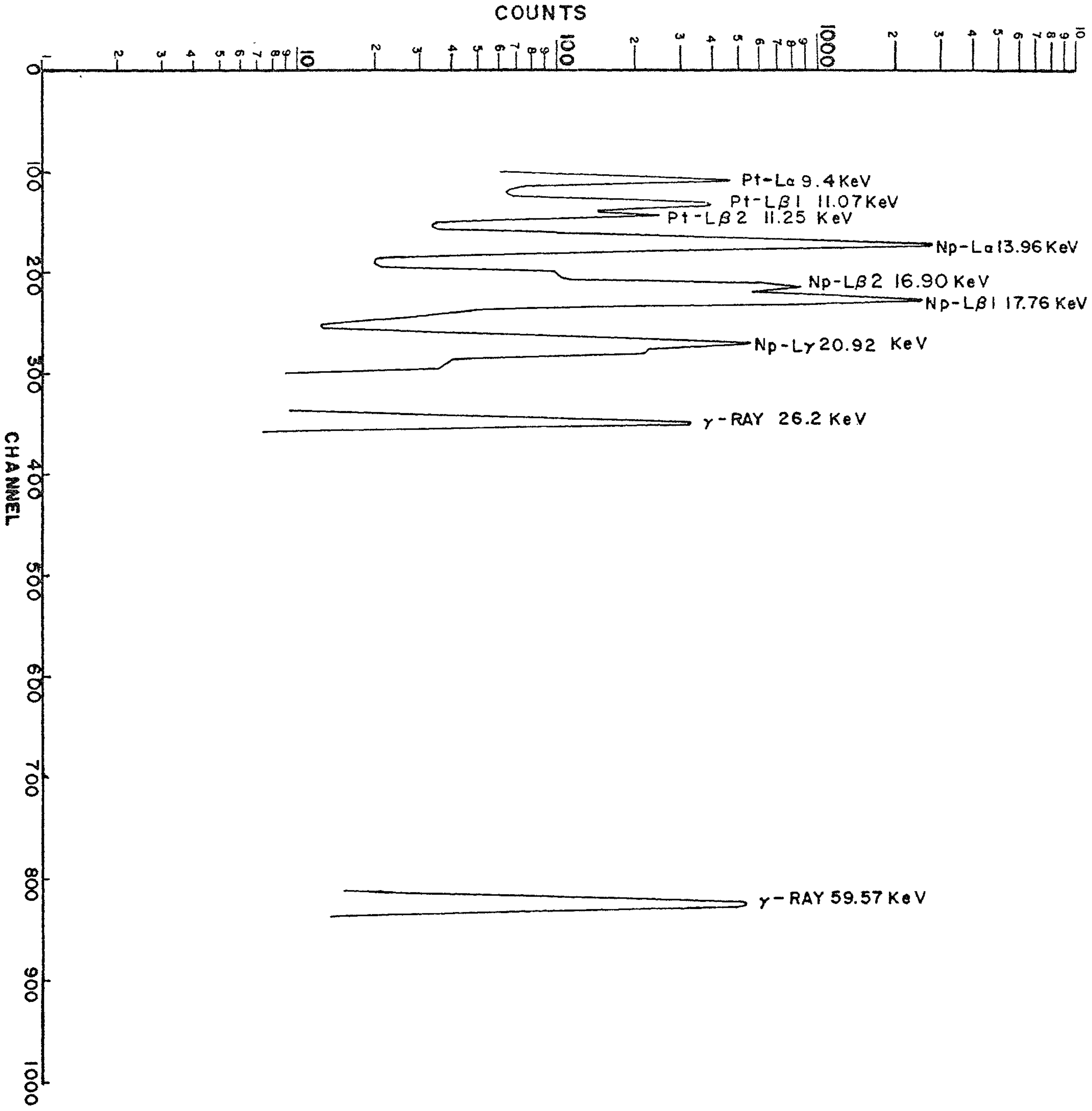


Figure 9. X-ray and gamma ray spectrum of ^{241}Am.

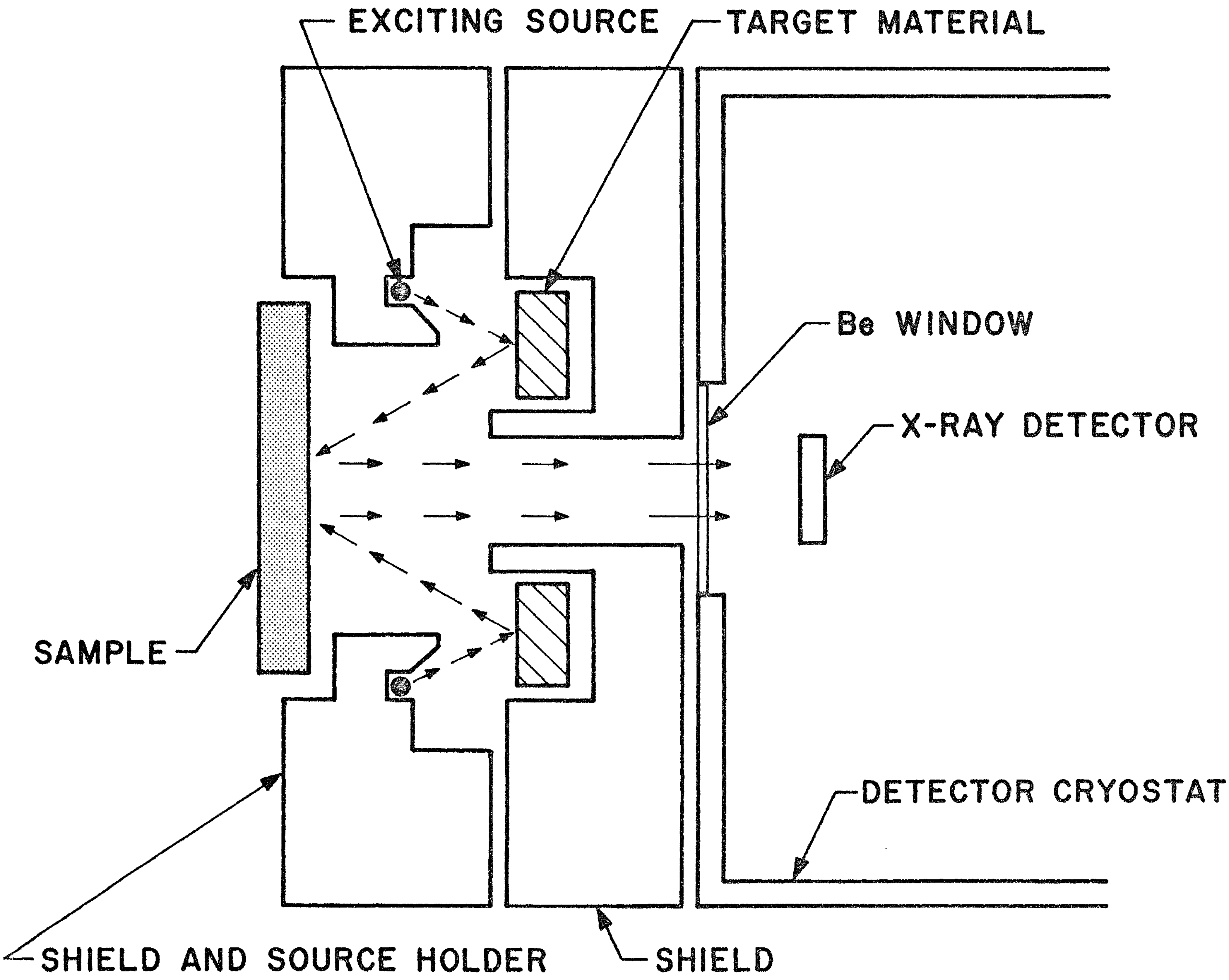


Figure 10. Schematic drawing apparatus for a two step excitation process.

If instead of doing the analysis in the above manner, one used a more intense ^{125}I source to excite a pure zinc target and then used the resulting zinc X-rays to fluoresce the sample, the iron K X-rays would be excited to a higher efficiency while the higher Z elements would only have their L X-rays excited, a lower efficiency process (G-5). Thus the background is reduced while the sensitivity is increased for determination of the iron content. This technique has both advantages and disadvantages. The disadvantages are the need for shielding the sample from the direct radiations of the source and the need for a more intense exciting source, perhaps as intense as 100 mc, to compensate for the decreased efficiency of this two step excitation process. The advantages are the increased sensitivity for detection of the particular element of interest, and the convenience of simply changing targets for different elements rather than changing radioactive sources. A schematic diagram of the above described device as suggested by Giaugue (G-5) is shown in Fig. 10.

D. Matrix Effects

In general, the quantitative measurement of trace elements in particulate matter by XRF is complicated by the presence of the surrounding atoms of the filter paper and the particulate matter. As a result, the X-ray intensity is not proportional to the quantity of material producing the X-rays. The two major effects causing this non-linearity are: 1) absorption of both the incoming exciting radiation and the emerging X-rays, and 2) an enhancement effect. The latter effect occurs when an X-ray produced in an element fluoresces a lower Z element. The intensity of the higher Z element will be diminished and the intensity of the lower Z element will be enhanced. This effect can introduce errors as large as 70% in the calculated concentrations (F-6). In most cases, however, the enhancement is roughly an order of magnitude lower than the absorption effect.

One possible way to compensate for these "matrix" effects is to use a standard whose composition is similar to the one being examined. However, constructing these standards is difficult, since nearly identical concentrations of the materials present in the original sample would have to be used in the standard if valid conclusions are to be drawn.

Several techniques to correct for matrix effects have been developed. Some of the more successful are the backscatter mathod (K-5), the extrapolation method (F-6), the dilution method (K-6), and fusion method (A-4). General descriptions of other methods can be found in references (A-4, L-5, & J-2).

Another approach is the semi-theoretical treatment of the problem (A-4, A-5, M-6, M-7, D-4, & S-30). Correcting for the effects of a polyenergetic source (such as the bremsstrahlung from the ^{147}Pm exciting source) is discussed in reference S-30.

In general, the nature of the material being examined (both the amount of bulk and the amount of the trace materials to be determined) and the precision desired determine which of the above techniques will be the most desirable. Successful application of the above methods can yield precision of better than 10% in concentration determinations. Since precision better than this is seldom required, matrix effects do not seem to be a serious drawback to the XRF method.

E. Ion Exchange Filter Papers in X-ray Fluorescence

The trace metal load of river water can be divided into its suspended and dissolved fractions. The division is made in regard to the size of the particles which contain the metals. A diameter of 0.45 microns is usually considered the lower limit for the suspended fractions. Anything smaller than this is the dissolved fraction. The dissolved fraction may be ionized or simply attached to a small particle.

In the load, a great variety of metals may be found. When the load is divided into its suspended and dissolved fractions, it is important to note that when considering strontium, boron, barium, zinc, copper, aluminum, manganese and iron, only for iron and aluminum does the concentration of suspended metals exceed the concentration of dissolved metals (K-9). For this reason, the study of dissolved metals is vital.

A method for collecting dissolved trace metals on backings suitable for XRF analysis involves the use of ion exchange filter papers. A number of workers have used these filter papers (C-5, C-6, C-7, S-28, S-29, B-7, B-8 & S-27) but none of these authors have dealt with concentrations as low as the parts per million range for water samples. However, sensitivities in the sub-ppm range have been achieved. Rose (R-1) has achieved a sensitivity limit of 25 ppm for several trace elements in actual water samples. The main difficulty in achieving lower sensitivities for water samples is the difficulty in passing quantities larger than 40 ml through the filter paper.

The first use of ion exchange filter papers was described by Grubb and Zemany (G-7). Ion exchange membranes have been used by Luke (L-4) however the papers appear easier to use and seem to present a more uniform sample for analysis.

The ion exchange filter papers are composed of approximately 50% cellulose and 50% ion exchange resin (C-5) which provides a matrix of low Z elements (C, H, O, N. S) which do not interfere with the XRF process. Standards for calibration are easily prepared by filtering solutions of known concentrations through the filter paper. Using Reeve-Angel (R-2) type SA-2 paper the following cations can be collected with better than 98% efficiency (C-5); Al^{+3}, Ba^{+2}, Bi^{+3}, Ca^{+2}, Cd^{+2}, Co^{+2}, Cr^{+3}, Cu^{+2}, Fe^{+3}; La^{+3}, Mn^{+2}, Ni^{+2}, Pb^{+2}, Sr^{+2}, Ti^{+4}, UO_2^{+2}, Y^{+3}, and Zn^{+2}.

Chapter IV Experimental Procedure and Results

A. Introduction

Using the apparatus and technique described in Chapter III, an investigation was made of the trace metals in outfalls and local water supplies in the Dayton area. Studies have also been conducted examining other samples for trace metals. Among the various samples that have been examined are human bones and hair, soil samples and samples of atmospheric pollution. The latter were collected on filter paper through which large volumes of air were passed (D-5, D-6, & B-9).

The work being reported here concerns trace metals in water samples. These samples were collected at the sites of interest using the closed container (S-33) shown in Fig. 11. A pressure of approximately 30 pounds per square inch was maintained in this device to force water through the filter paper in the bottom by using a bicycle pump. The filter paper was supported by a stainless steel mesh (Millipore Cat. #XX2004708). The paper was Millipore type SCWP 04700 with 8μ and 0.45μ pore sizes. This procedure eliminated the need for carrying large containers of water back to the laboratory. It also shortened considerably the time that the water being sampled was in contact with a different environment. Thus, the samples collected had little chance to be contaminated by the collection device. This procedure also reduced the possibility of the container absorbing the elements of interest from the water. The filter papers thus prepared were immediately ready for analysis by XRF.

This chapter describes procedures followed in the present work for measuring qualitatively and quantitatively the amounts of trace metals on the filter paper. Also described are the accuracy, sensitivity and characteristics of XRF.

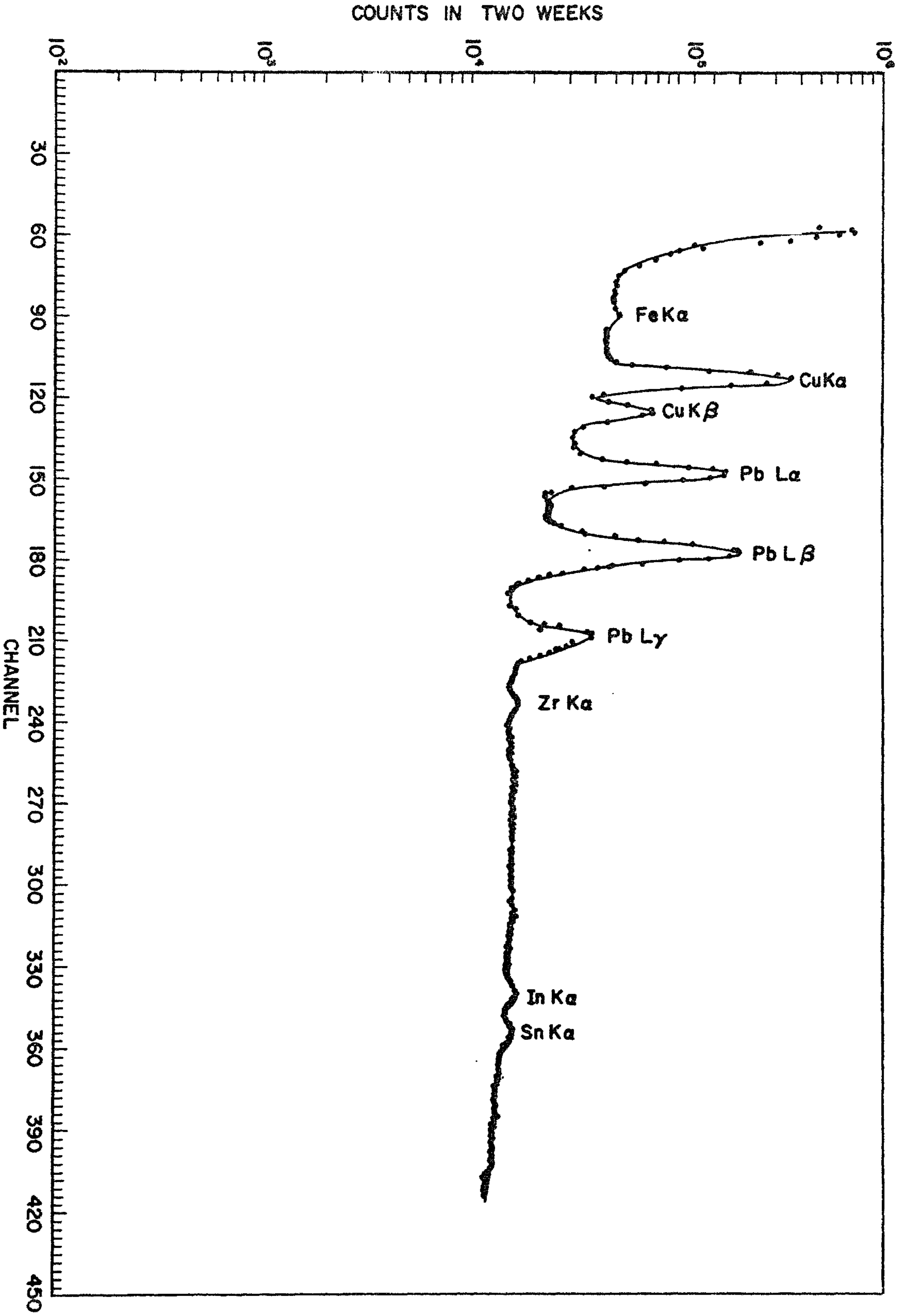


Figure 12. X-ray fluorescence spectra of a blank Staplex filter paper (a lead shield was used).

B. Qualitative Measurements

In the early part of this work, elements were identified by determining their energies and consulting a table of X-ray energies for the various K and L lines. As the stability of the detector and electronics was to within one channel in general on the multichannel analyzer, this procedure seemed good enough. However, over the long run some electronic drifts occured and periodically power failures provided shifts in calibration when the equipment was turned back on. A relay was installed in the main power system for the equipment so that when the power came on after a power failure, the equipment did not. The voltage on the detector was then increased slowly. This procedure reduced the possibility of gain shifts. However, the most reliable and positive method for element identification is to run standard samples of the suspected elements. This can be easily and quickly done by having a set of salts or foils of probable elements and fluorescing them after the sample has been analyzed. If the elements being analyzed are the same for several samples, this procedure need be done only once and after that the spectra itself can be used for energy determination (element identification). In general, it is important to have available standards of several elements to make positive element identification.

Several filter papers were analyzed for their trace element content and the only ones which were satisfactory for XRF work were Watman #41 and Millipore papers in general. Their trace metal content was negligible for the metals of importance in this work. As examples of this problem, the trace element contamination in Staplex paper filters is shown in Fig. 12 and contamination in a glass fiber filter is shown in Fig. 13. Fig. 12 was produced using a lead shield for the exciting source so the lead peaks are due to fluorescence from the shield. The copper peaks in Fig. 13 are due to the bronze shield used in the collection of that spectra. It should be noted that the bronze shield

APPARATUS FOR RADIATION FIELD SURVEY

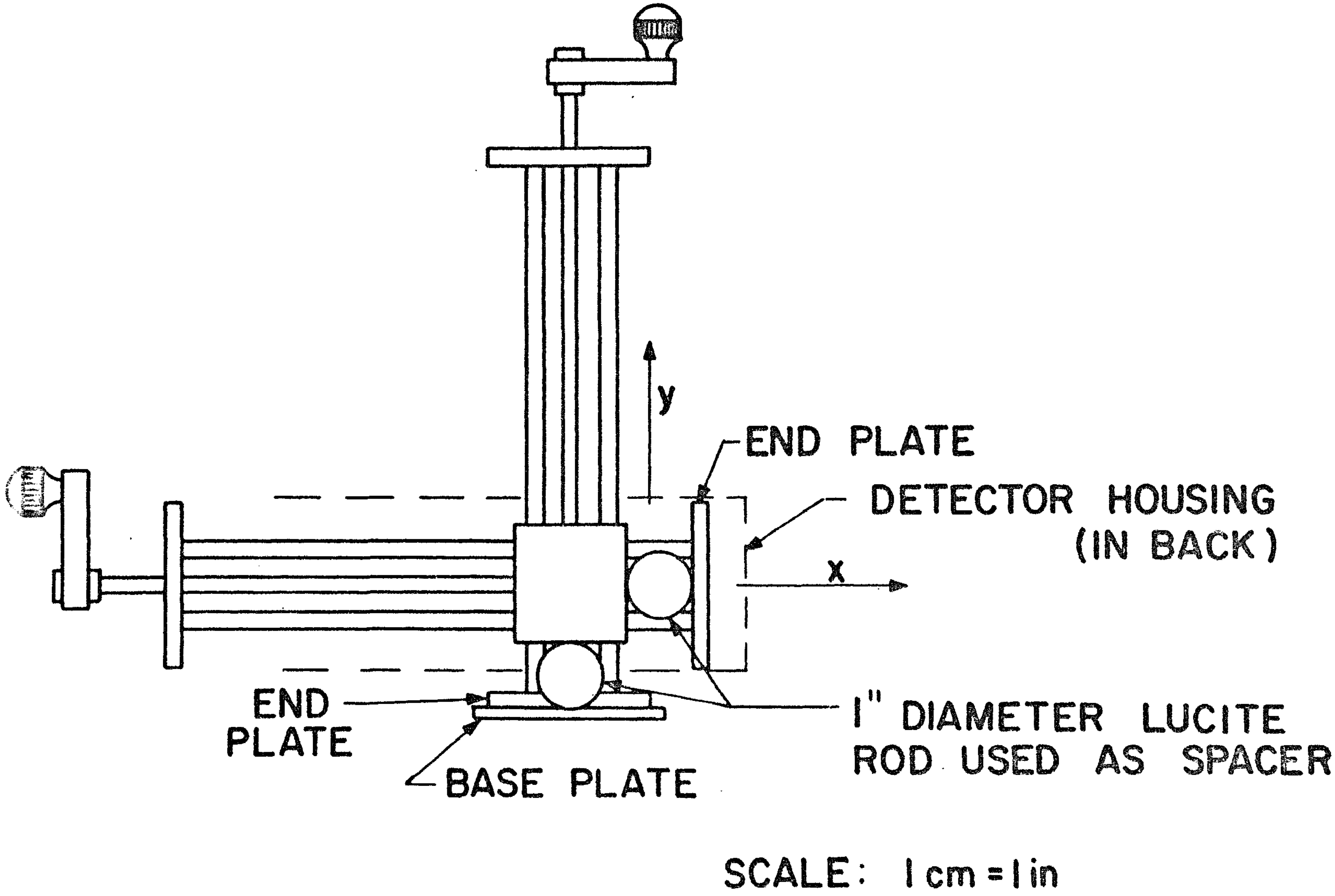


Figure 14. Device fabricated to move a "point sample" of solder through the sample region in small steps of space.

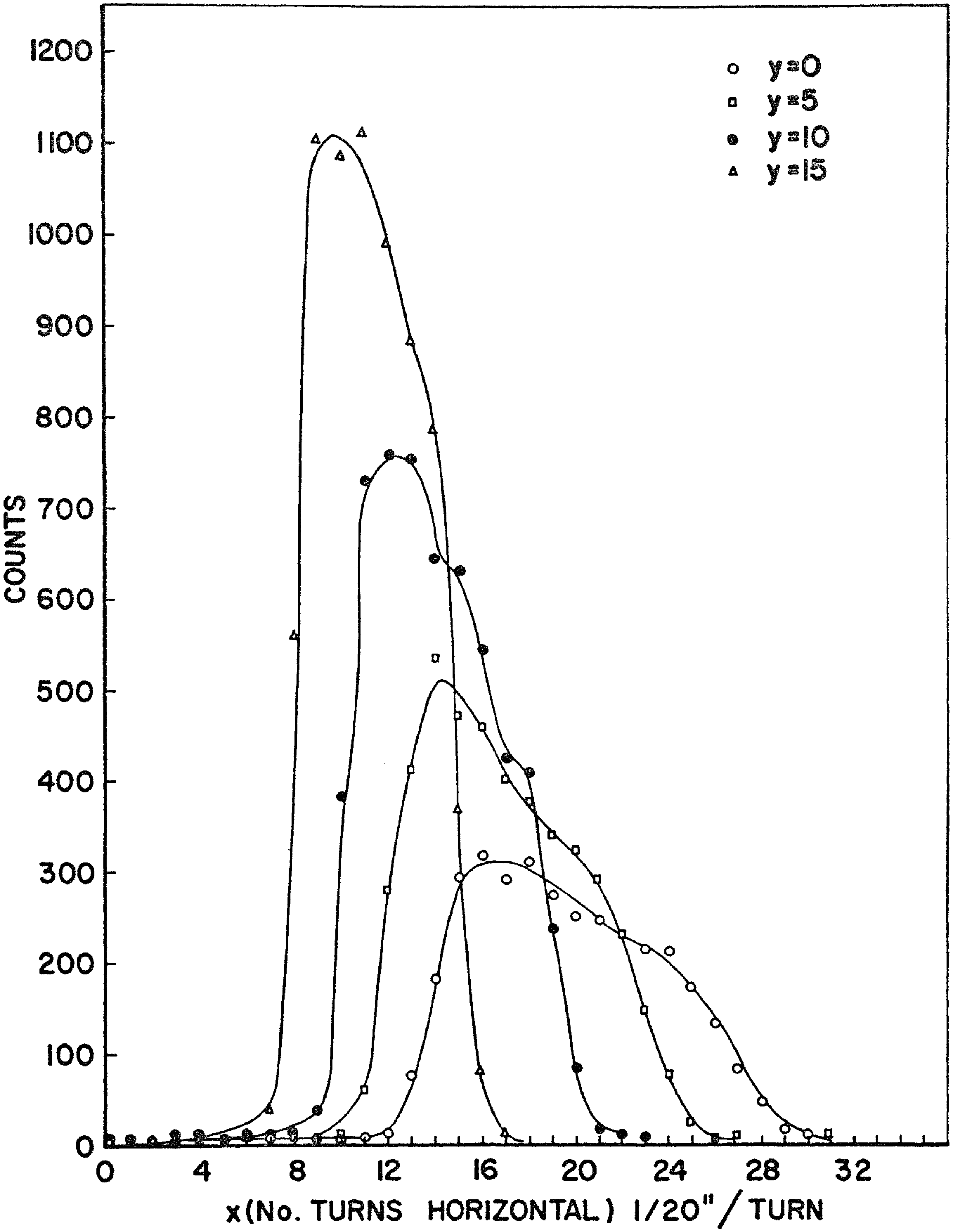


Figure 15. variations in the radiation field as a function of X and Y displacement in the sample plane.

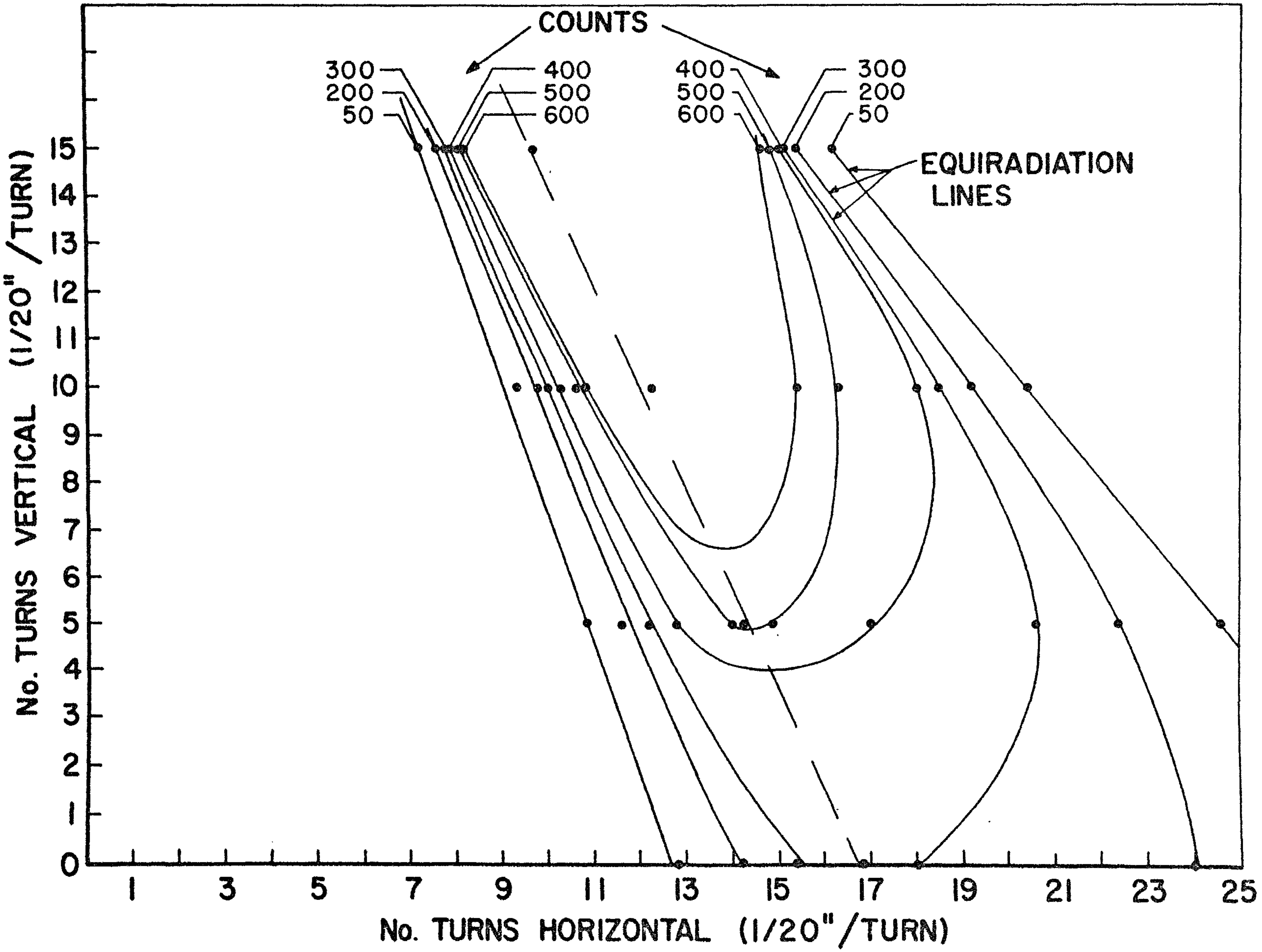


Figure 16. Equiradiation lines describing the radiation field at the sample position.

yielded less background than the lead shield by about a factor of two when they are normalized to the same time period. As copper was of more interest in this work than lead, the lead shield was used. Also the copper peaks were large enough to obscure the peaks from other elements in the sample in that energy region while the lead L peaks occurred in a region of the energy spectrum (see Table II) where not too many elements of interest occurred (although the X-ray peaks of neighboring elements in the periodic table were resolvable, when one element produced a very intense X-ray peak it did not interfere with the determination of neighboring elements).

C. Uniformity of X-ray Field and Accuracy of Method

It is important to know the relative strength of the radiation field over the sample region in order to determine where to place the samples. To achieve this measurement, a screw type device was constructed which could move a point sample through small distances in the x and y direction in the sample plane. A drawing of this device is shown in Fig. 14. As can be seen from the dashed lines in this figure, the detector is just behind the device. A small bead of solder was put on the end of a screw on the end plate of this device so as to locate the radiations. The K_α peak of tin from the solder was used in mapping out the radiation field. The data for different x and y positions of this bead is shown in Fig. 15 while the equiradiation lines are shown in Fig. 16. These equiradiation lines are useful in determining the size and placement of the sample.

Another approach to the problem of determining the extent of the radiation field presented at the sample produced by the exciting source was through the use of different sized samples. Copper was vacuum plated on aluminum backings by using masks with several holes of from 1/16" to 1" over

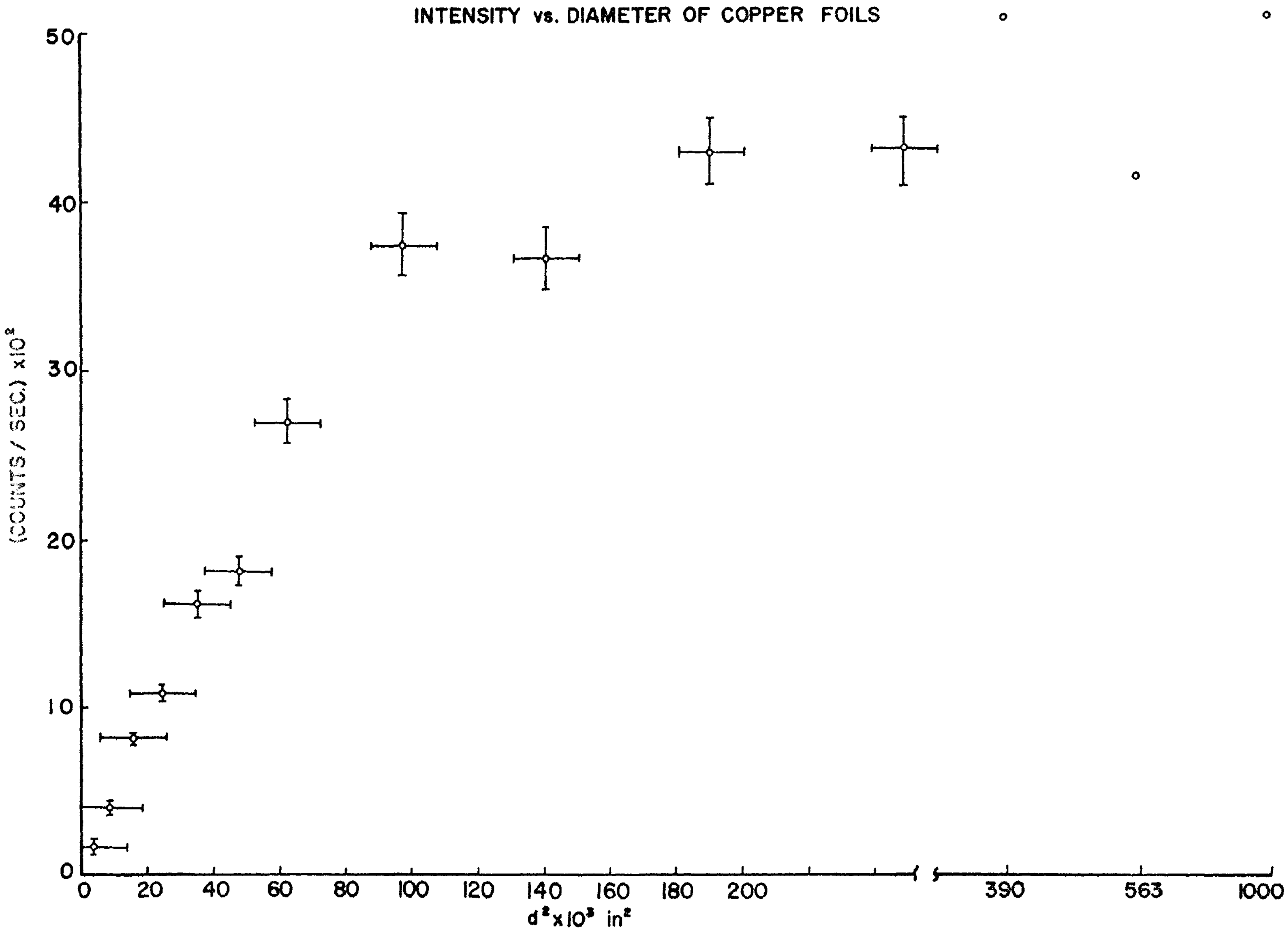


Figure 17 X-ray intensity as function of sample diameter using copper discs evaporated on aluminum backings.

the aluminum during the plating process. During the evaporation process, the foils were kept far enough away from the copper source (more than 12") to insure that the thickness of the copper on each part of the aluminum was constant. As can be seen from Fig. 17, the relation between fluoresced counts and diameter of copper is fairly linear until the diameter reaches about 1/3" at which point the curve levels off. Thus if a sample is larger in diameter than 1/3", the count rate will increase only slightly from the value at a diameter of 1/3". That is in order to eliminate the problem of reproducibility of sample position, the sample needs to be larger in diameter than 1/3". Due to considerations involving the available size of commercial filters (mainly those of the Millipore Co.), and diameter of 1 3/8" was decided on to provide a sample that was uniform and large enough to reduce the above discussed geometry problem.

In order to show the accuracy and sensitivity of XRF, a study was made of the peak intensity as a function of sample weight. A 100 ml solution of Cu and Sn were prepared from 105±0.1 mg of $SnCl_2 \cdot 2H_2O$ and 197±0.1 mg of $CuSO_4$. This produces a 500 μgm/ml concentration of both Cu and Sn. The solutions were further diluted by water to produce 100 μgm/ml and 10 μgm/ml solutions. These solutions were then evaporated on 1/2" diameter Watman #41 filter paper. In order to prevent the Cu or Sn from flaking off the filter papers, they were covered with Scotch tape. In order to eliminate centering problems each sample was run twice, the second run being with the sample rotated 180° with respect to the first. The data from this work is shown in Table V and is presented in Fig. 18. As can be seen, the system is linear to 10% over the range of interest. The errors shown are due to both background and statistics. The intensities

Table V

Table of study of sensitivity and accuracy of XRF using Cu and Sn samples

Weight (Micrograms)	Counts/secx 10^{-3} Copper	Tin
100	73.3 ± 6.5	269 ± 21
70	54.7 ± 6.8	277 ± 20
70	70.5 ± 6.5	217 ± 16
50	37.0 ± 5.6	139 ± 16
50	42.1 ± 5.0	135 ± 12
30	28.8 ± 4.5	60.6 ± 9.2
30	18.4 ± 3.7	60.9 ± 10.2
10	7.85 ± 1.4	31.7 ± 5.3

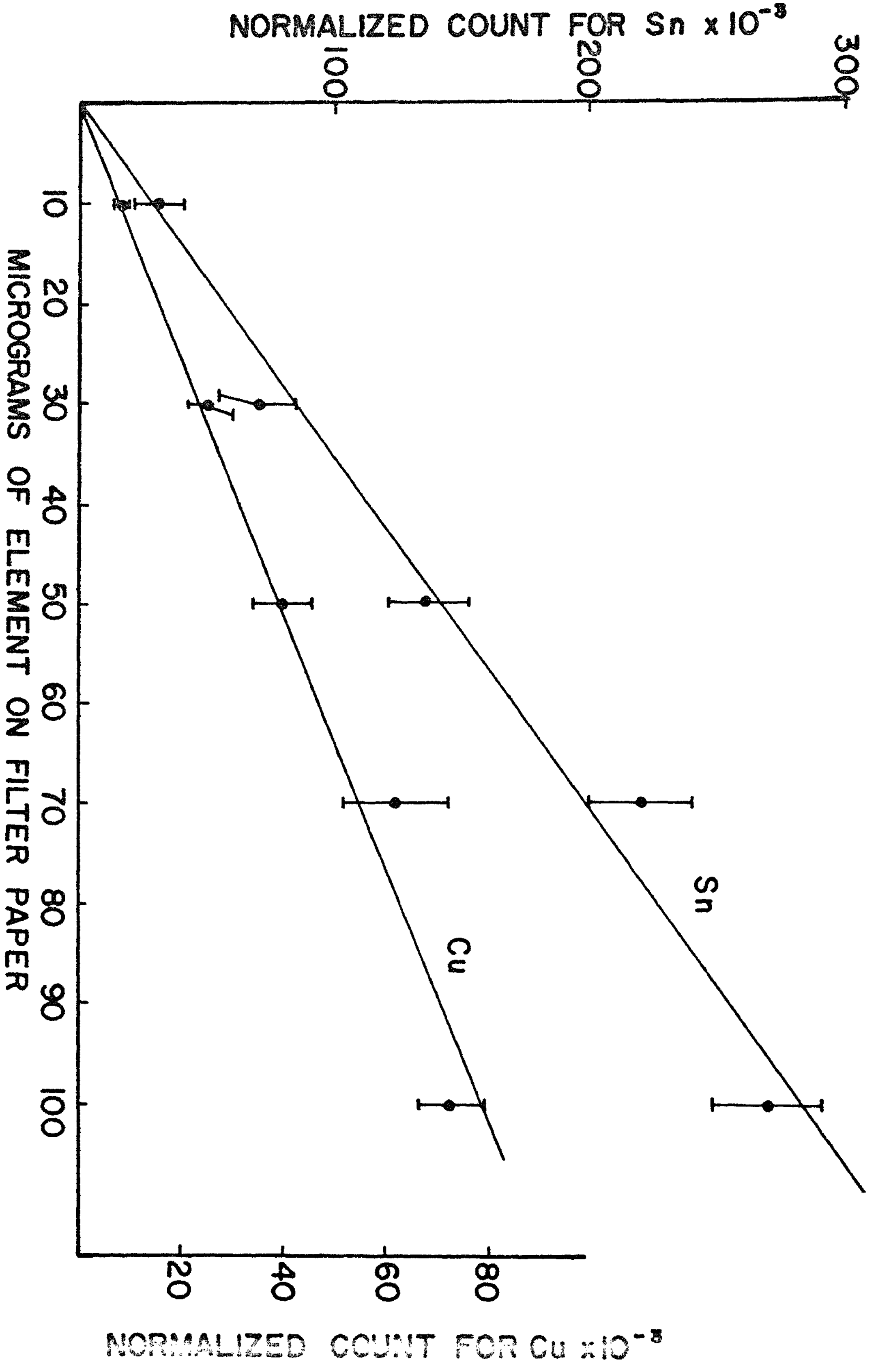


Figure 18. Graph showing the sensitivity and accuracy of XRF over the mass range of interest.

of the peaks were obtained by summing the total counts under the peak and subtracting the background. The error from statistics was the square root of the number of counts. The error of the background was estimated by drawing the maximum and minimum background lines above and below the line chosen as background. The error in the background was then taken to be 2/3 of the difference between the background chosen and the maximum or minimum background.

D. Quantitative Measurement

The main problems inherent in the development of a procedure for the quantitative determination of elements by XRF are

a. the uniformity of the X-ray field

b. the reproducibility of the sample geometry

c. the preparation of standards and the determination of an efficiency curve

d. the background-sample composition and backing material.

Point d was discussed in general in Chapter III, and further investigative work in this area is the subject of future work in our laboratory. Points a and b were discussed in section C of this Chapter.

In order to quantitatively calibrate the apparatus thin foils were tried. However as shown by Fig. 19, the foils tried were too thick. This is shown in the figure by the same intensity for both single and double thicknesses to Ti (each 0.001" thick). A simple calculation shows that the foils need to be thinner than those commercially available. In fact, the foils would have to be so thin that they could not stand unsupported. For example, consider some metals of interest; Fe, Ag and Sn. For all these metals the absorption coefficient is similar and about 500 cm^2/gm (G-3). The density of these three metals is around 8 gm/cm^3 (at the iron K

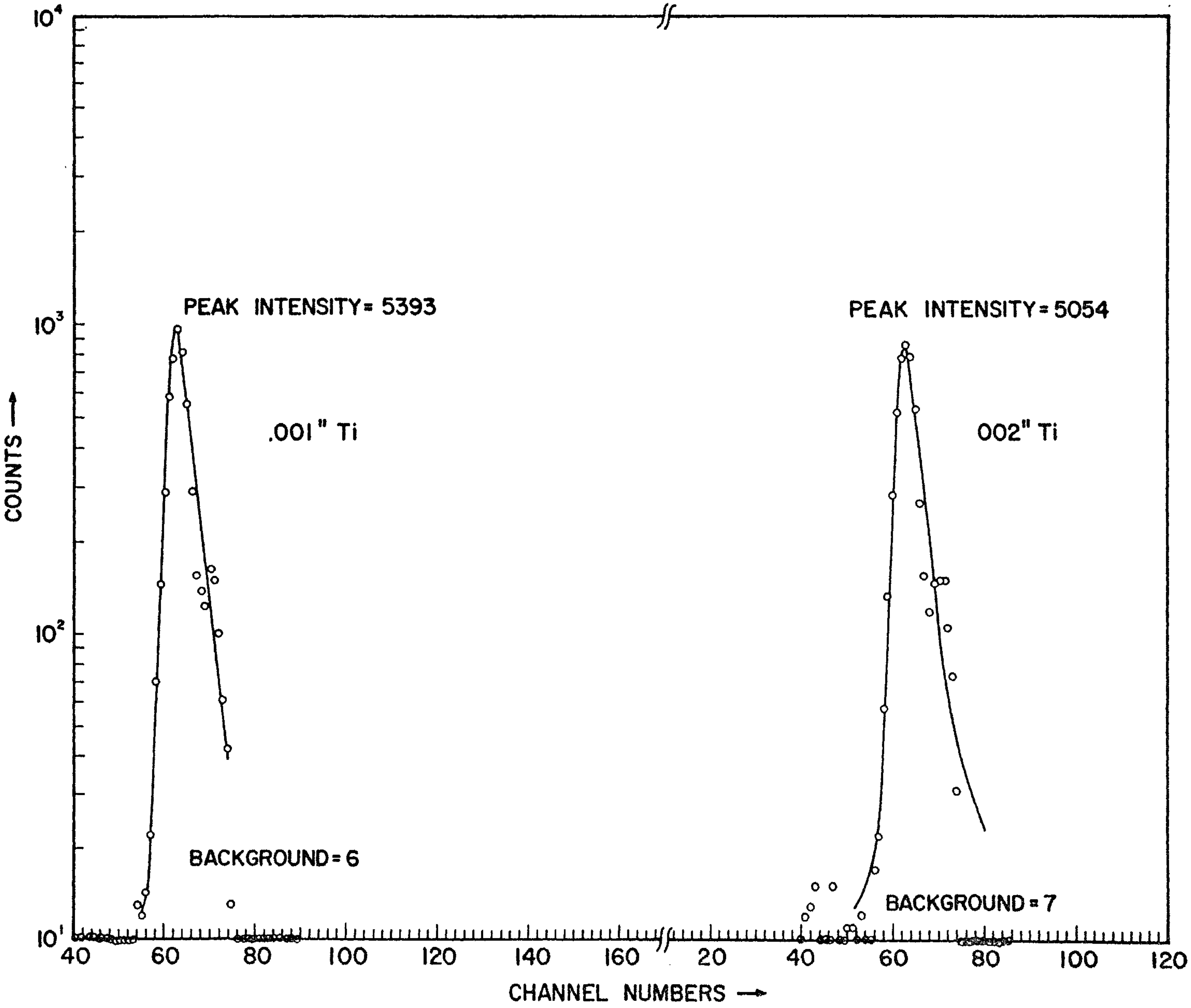


Figure 19. Comparison of Spectra produced by fluorescing single and double thicknesses (each 0.001" thick) of titanium.

X-ray energy). At the iron X-ray energy a 0.175 x 10^{-3} cm(17,500 Å) foil would reduce the X-ray intensity by 50% and a 0.026 x 10^{-3} cm(2600 Å) foil would reduce the intensity by 10%. Thus the use of thin unsupported foils to quantitatively calibrate XRF apparatus is not practical. To produce thin layers of the metals of interest, the technique of vacuum deposition was tried.

Known samples for calibration were made by vacuum depositing the metals of interest on aluminum foil. Amounts deposited ranged from about 100 ug to 6000 ug of some of the heavier metals. The metals were deposited on the foils in disks of 1 3/8" diameter which eliminates centering problems in the XRF apparatus since the radiation field is much smaller. Deposition was done by a Veeco VE-400 Vacuum Evaporation Unit. Tungsten coils and filaments were used for evaporating manganese, silver, yttrium, and zinc while a tantalum coil was used for tin. An aluminum template with a 1 3/8" circular hole was used to cover the aluminum foil during plating. The current and vacuum varied with the metal being plated. Metals with higher evaporation points (see Table VI) required a better vacuum and more current. The vacuum was generally on the order of 10^{-6} mm Hg in the bell jar and current ranged from 40 to 80 amps.

Table VI

Metal	Evap Point (°C)
Tin	1189
Silver	1047
Yttrium	1649
Manganese	980
Zinc	343

Because the disk of metal plated on the foil had to be uniformly thick, the foil was placed about 12 inches from the filament. It was necessary to use several hundred times the amount desired on the foil because much of the evaporated metal plated onto the glass and floor of the bell jar.

In order to calculate the quantities deposited, the foil was weighed before and after plating, on a semimicro-balance with accuracy to 10^{-5} gm.

Several samples of each metal were plated and analyzed for 10,000 sec. The intensity of the peak varied linearly with the thickness of the metal, provided the layer was thin enough that self-absorption was negligible. For a constant cross-sectional area, the thickness was directly proportional to the volume, so intensity was proportional to the amount of metal present. Since the relationship between amount and intensity was known to be linear, a straight line plot was calculated by the least square method for each metal (see Fig. 20-24). From each of the plots in Figs. 20-24, the count rate for a given amount of metal can be determined. The number of atoms not the mass must be the constant and 5×10^{-6} moles was chosen arbitrarily. The relationship between this number of atoms and mass is shown in table VII. As shown in the plots, these masses determined the count rate for 5×10^{-6} moles which when plotted as a function of energy (or Z) gave an overall efficiency curve (Fig. 25). This efficiency curve was then used to quantitatively determine the amount of each metal present. The data for this procedure is shown in Table VIII along with the equations for the least square fits and the standard deviations in the counts. The standard deviation is the square root of the sum of the squares of the differences between given points (counts) and the value according to the calculated lines.

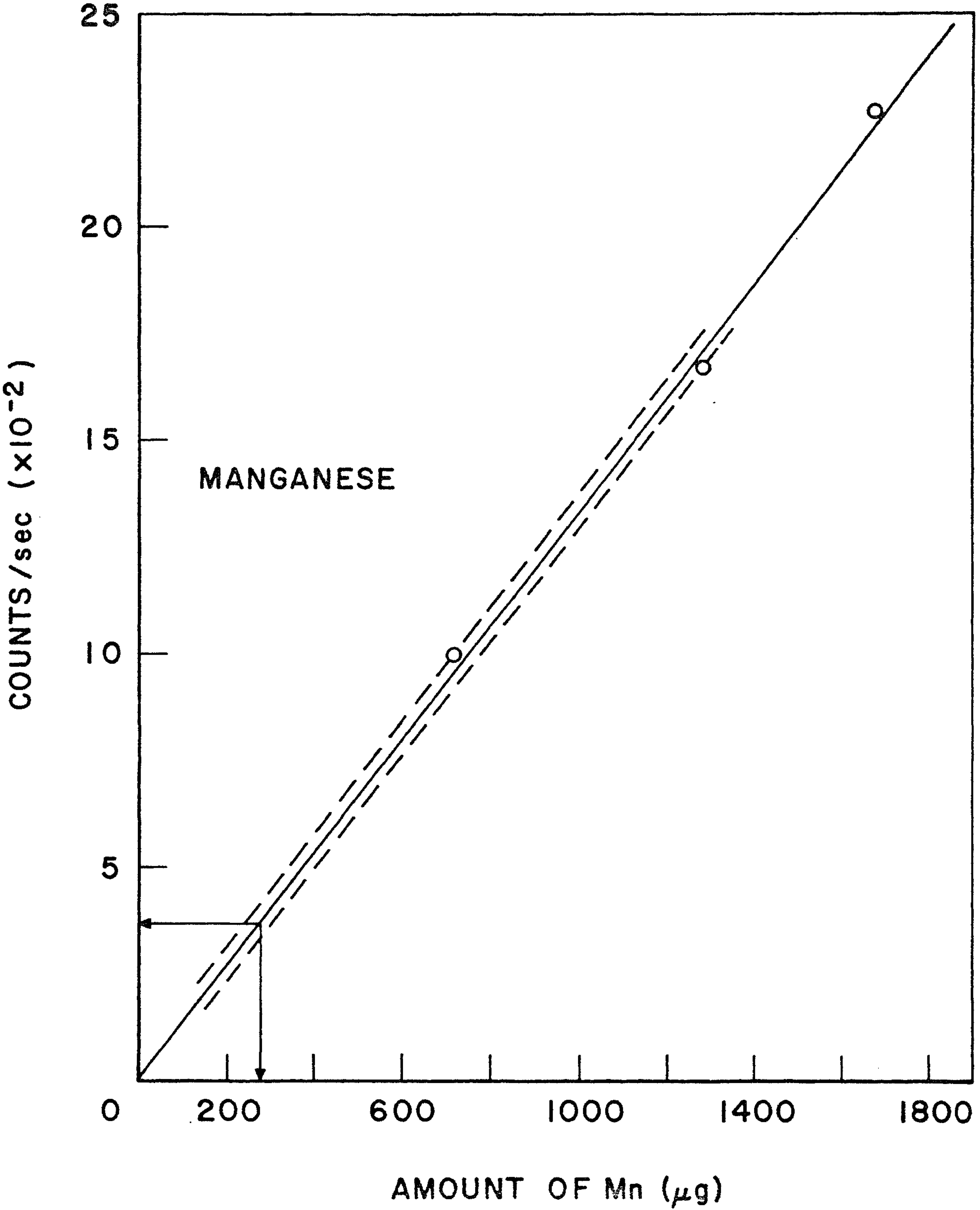


Figure 20. Manganese calibration plot.

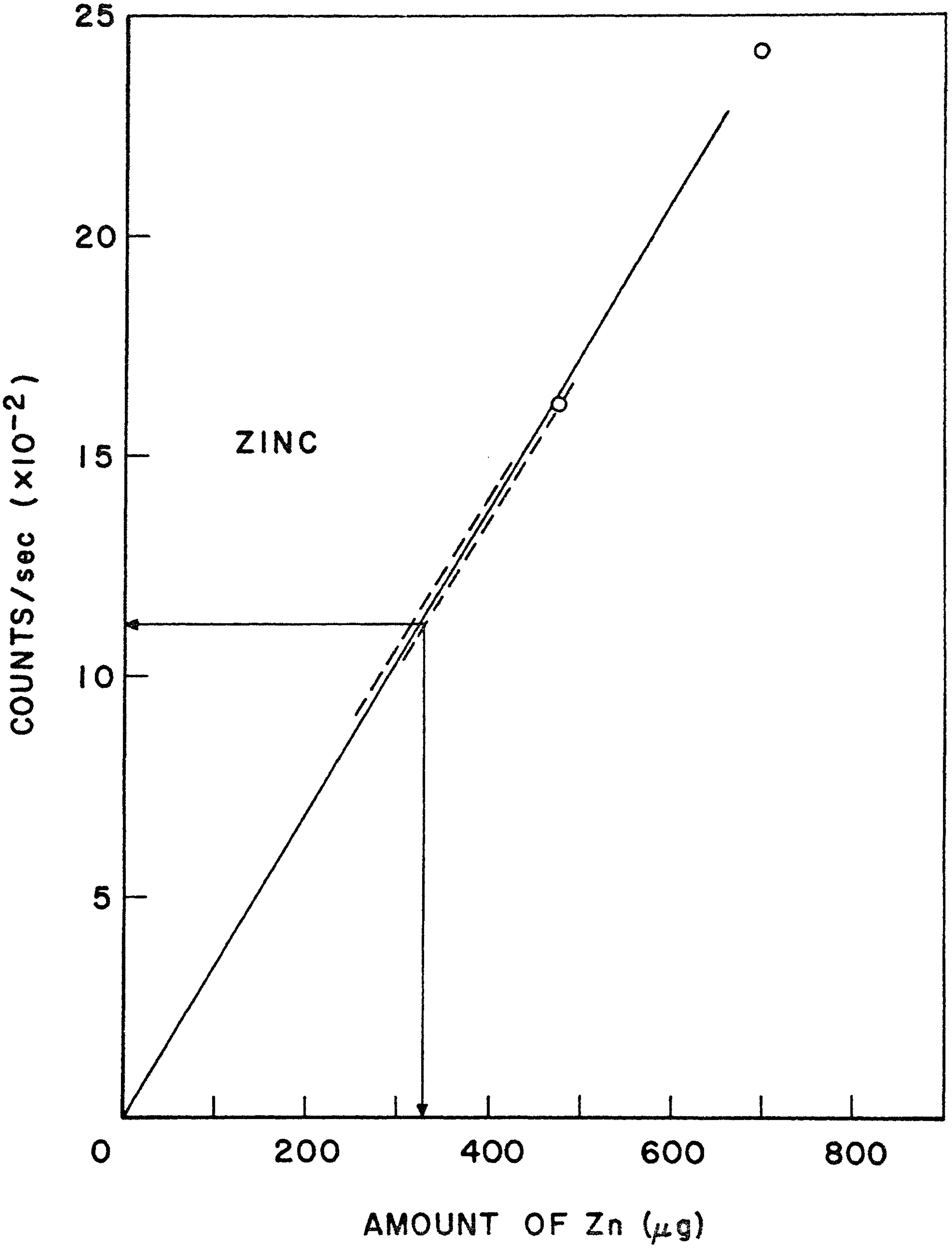


Figure 21. Zinc calibration plot.

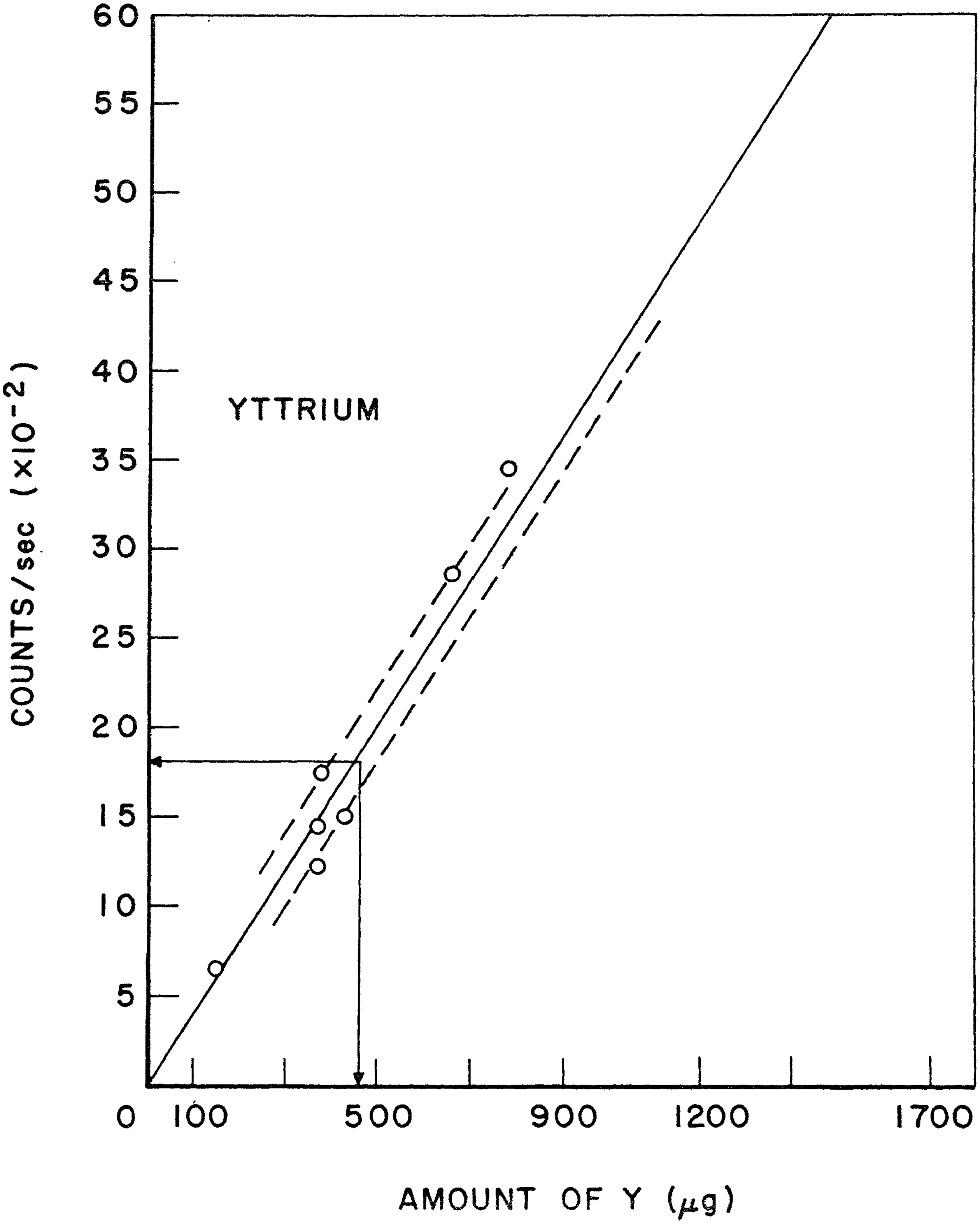


Figure 22. Yttrium calibration plot.

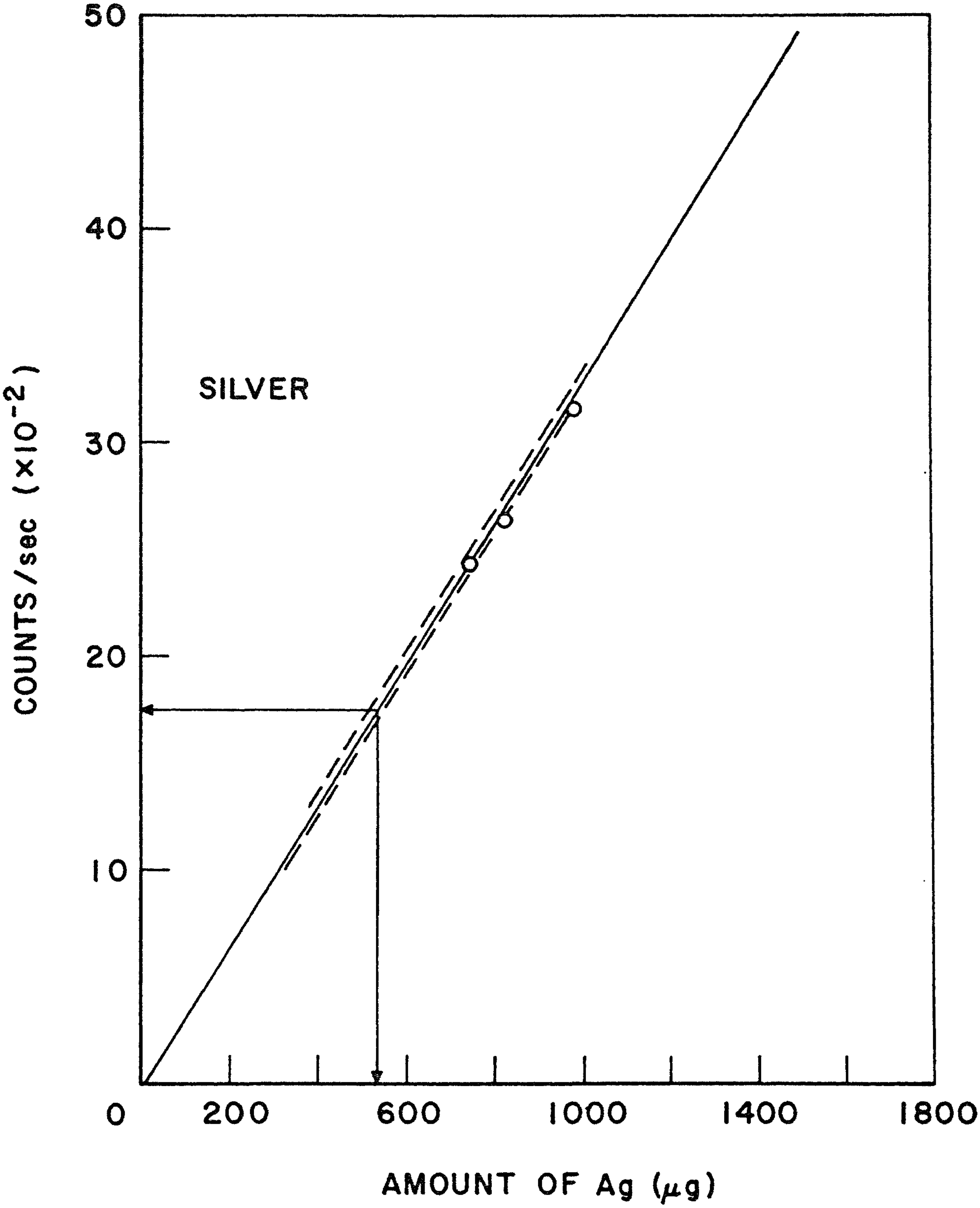


Figure 23. Silver calibration plot.

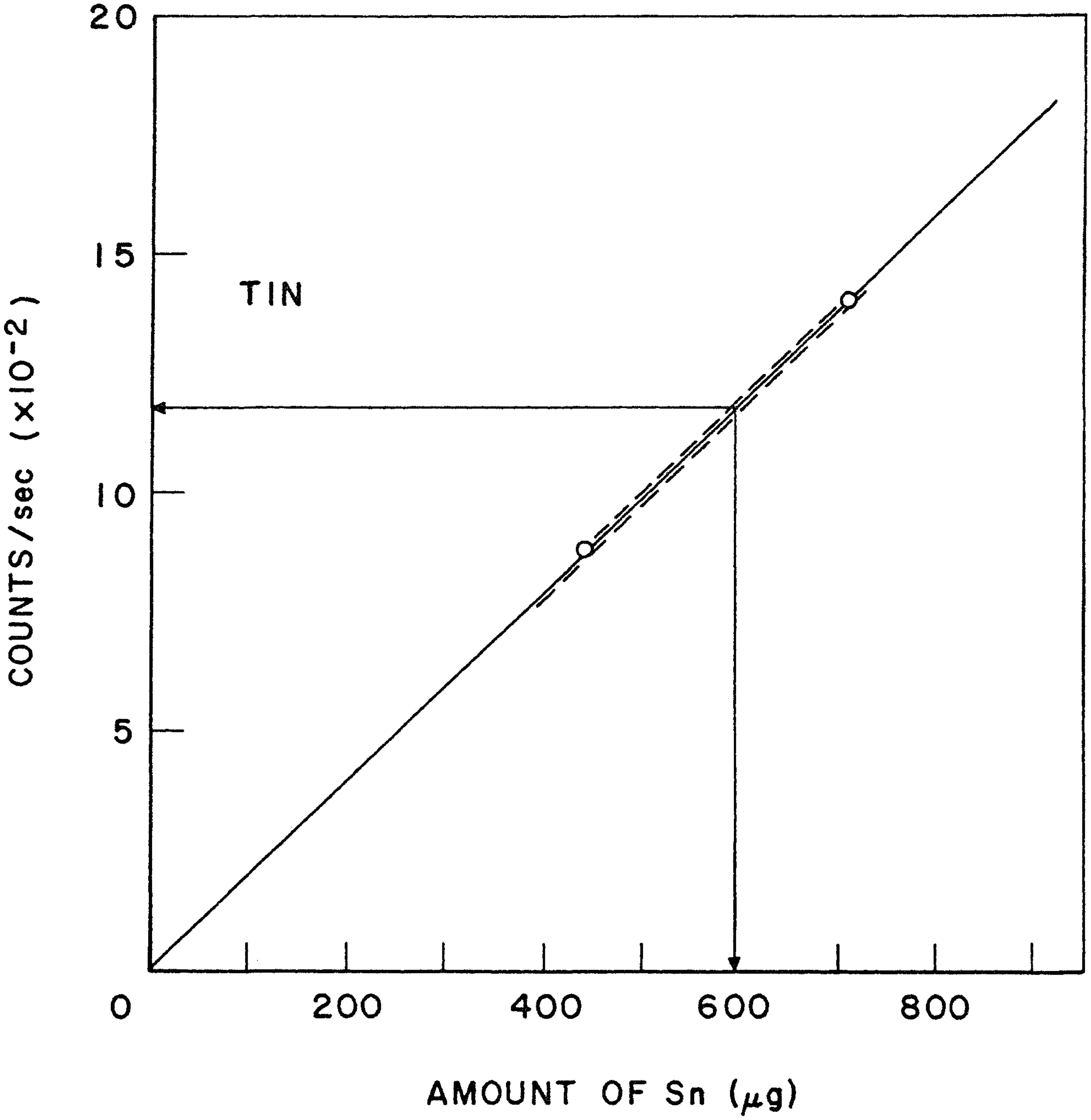


Figure 24. Tin calibration plot.

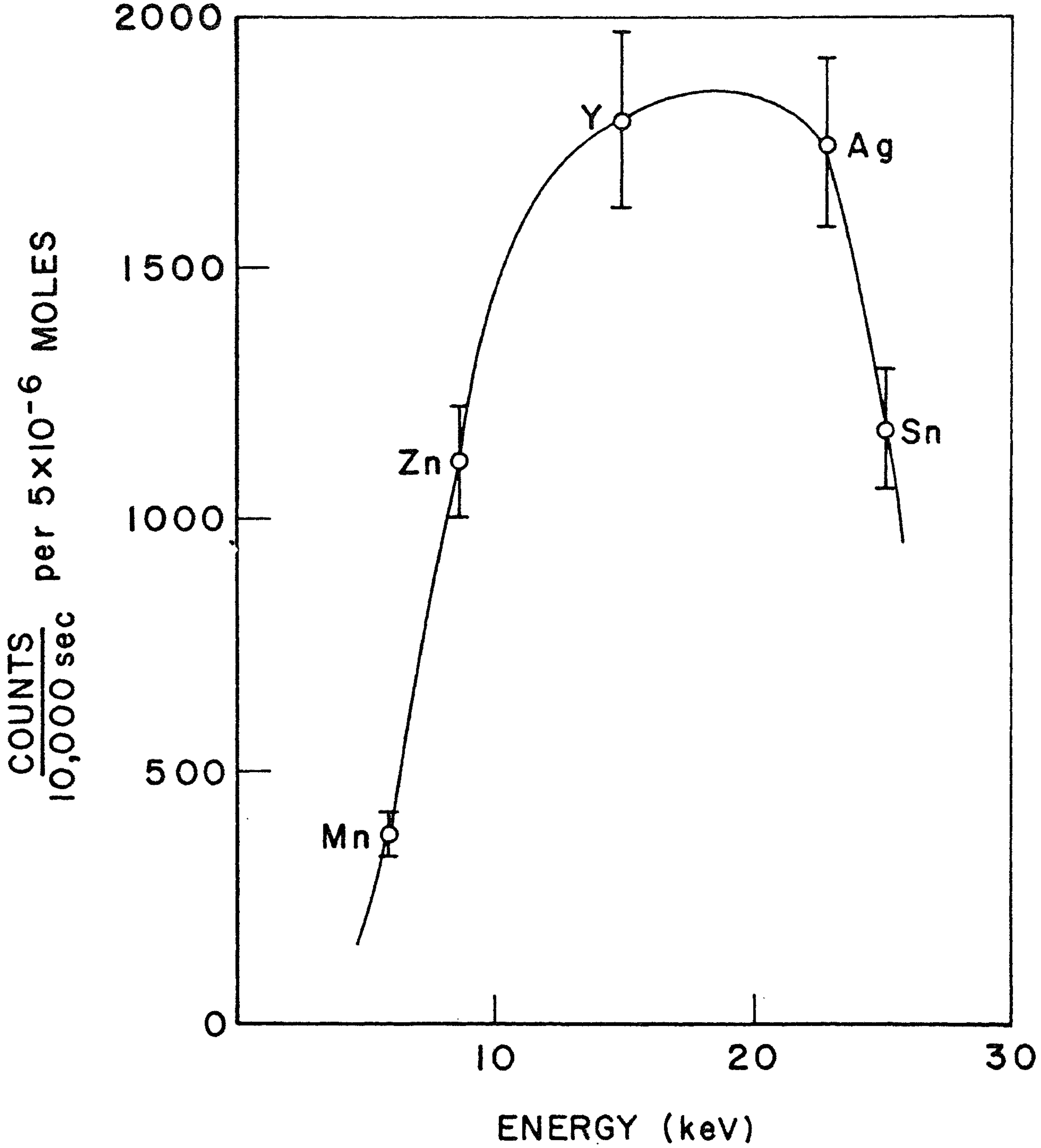


Figure 25. Efficiency curve for the apparatus used in the present work.

Table VII

Element	Atomic Weight (amu)	Mass of 5 x 10^{-6} moles (ugm)
Mn	54.93	274.6
Zn	65.38	326.9
Y	88.9	444.5
Ag	107.9	539.4
Sn	118.7	593.5

Table VIII

Metal	$\frac{\text{Counts}}{\text{10,000 sec}}$	amt of metal (ug)	linear relationship	standard deviation for counts/10,000 sec
Silver	2414	740	$\text{amt} = \frac{\text{cts/10,000 sec} + 29}{3.29}$	37.0
	2632	820		
	3155	980		
	5275	1600		
Manganese	993	720	$\text{amt} = \frac{\text{cts/10,000 sec} - 5}{1.33}$	38.7
	1668	1290		
	2267	1680		
Yttrium	640	150	$\text{amt} = \frac{\text{cts/10,000 sec} + 3}{4.05}$	202.2
	1206	370		
	1490	430		
	1441	370		
	1744	380		
	2857	660		
	3447	780		
	6317	1590		
Tin	1401	710	$\text{amt} = \frac{\text{cts/10,000 sec} - 3}{1.98}$	6.7
	880	440		
Zinc	1615	480	$\text{amt} = \frac{\text{cts/10,000 sec} + 10}{3.44}$	22.8
	2758	800		

E. Method of Error Analysis and Sensitivity

Full peak width at half maximum was found to average 5 channels, so intensities were calculated from a 10 channel width. Background was found by averaging the counts in the 10 channels immediately preceding the peak. The three smallest counts in these 10 channels are averaged and the square root of this average is the standard deviation. If 2/3 of the 10 counts used for background are within one standard deviation of the average, then that is taken as background for the peak being analyzed. If, however, 2/3 are not within a standard deviation, 10 channels immediately following the peak are used in the same procedure. If these, too, are not in statistical range, then 10 channels are again taken from before the peak by moving 4 channels back and picking up 4 new channels. The process is repeated until a suitable background is found. This method was found to be best in eliminating the possibility of using the peak of a second element, or the K_β peak of the same element for background. Once background is calculated, it is subtracted from counts in the 10 channel peak of the element being analyzed. This result is used to calculate counts/sec, by dividing by analyzing time. This time is usually 10,000 sec for known samples and 40,000 sec for unknown.

The total error includes the background error, peak intensity error, and the error accumulated in the least squares fit used for calibration metals. Background error is taken to be the standard deviation of the ten channels used, and has been calculated from the smallest three values during the process of finding background. The peak intensity error is the square root of the total counts less background. These errors combine to give the error in the efficiency curve (see Fig. 25). In general, an overall error of 10% is to be expected for most metals.

When a water or air sample is analyzed, the trace metals present can be identified by the channel number of the peaks. Background must be found for each peak because it varies over the 1024 channels. Intensity of each peak is then calculated. Since calibration was done with 10,000 sec runs, calculations are done in this form. If the element being analyzed is one of those used in calibration, the linear equation is used to calculate amount present on the sample. If it is another element, the relation can be read from the efficiency curve which gives counts/(5 x 10^{-6} moles x 10^4 sec) or counts/(at. wt. x 5 x 10^{-6}g x 10^4 sec) or counts/(at. wt. x 5 ug x 10^4 sec). Thus the amount of metal present is determined. By knowing the quantity of water analyzed, the ppm value can be ascertained.

Statistics put a limit on the minimum amount of trace metal detectable. The standard deviation from counting statistics is given by the square root of the number of counts. Letting the number of background counts be B then $3\sqrt{B}$ was arbitrarily chosen as the sensitivity limit. That is, the height of the peak must be at least $3\sqrt{B}$, to be considered detectable. Using average background counts found in unknown samples containing several metals, sample minimums were calculated and are listed in Table IX. Since intensity and analysis time determine μg of metal, the limits are in μg. The actual ppm value depends on volume of water. Sensitivity limits for a similar experimental setup using a 10 mc of ^{125}I source were 35ngm for Mo and 1μgm for Ni (Y-1).

F. Use of Ion Exchange Filter Papers

The need for using ion exchange filter papers to collect the dissolved metals on water samples was discussed in Chapter III. The preliminary work reported here concerning the use of ion exchange filter papers involved the determination of several factors which promote the efficiency of ion exchange resin (W-4). The percentage of ions collected by the papers is a function of the pH of the solution in which the ions are exchanged. A pH of 2 was found

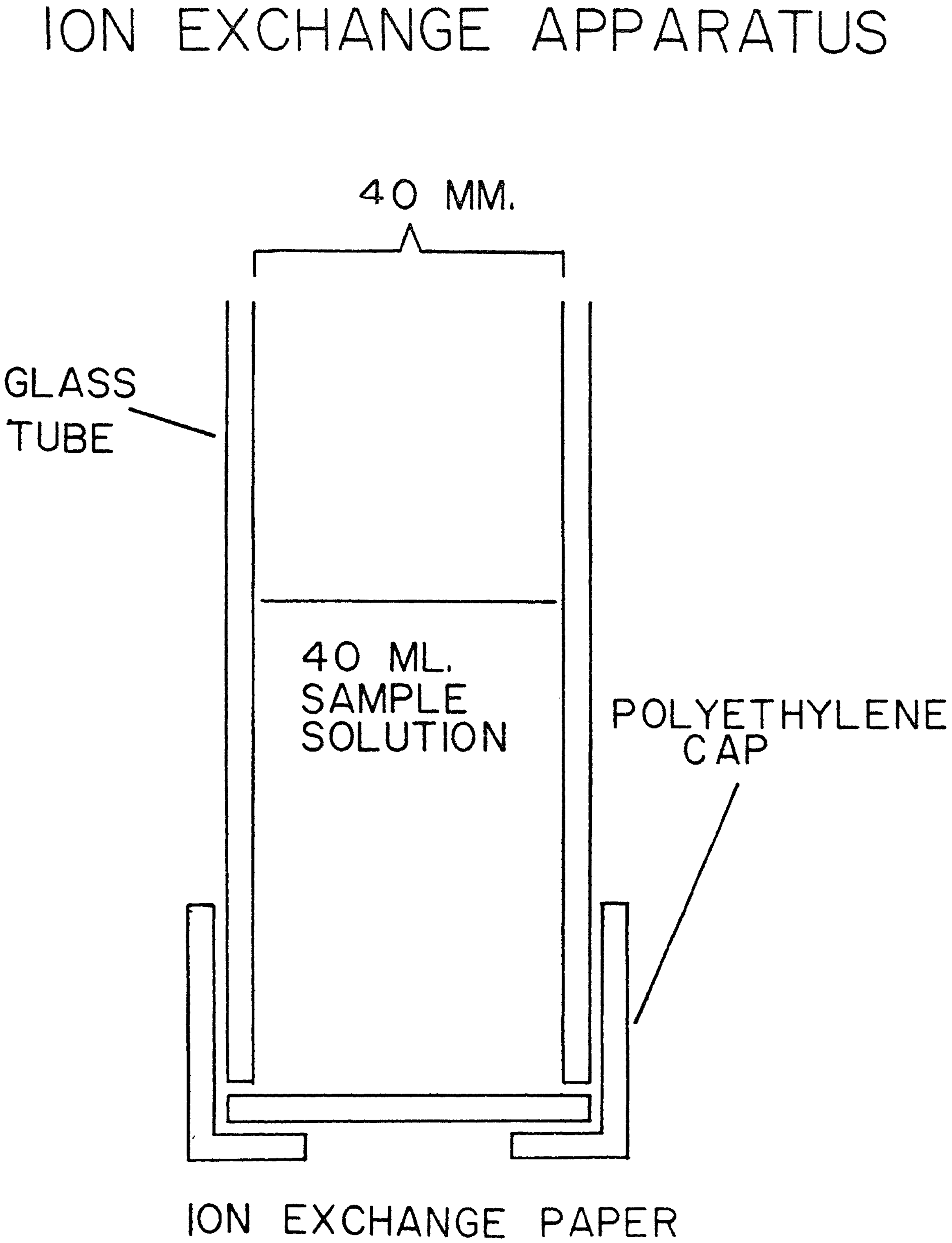


Figure 26. Apparatus for use with ion exchange filter papers.

to be the most efficient (C-6). Furthermore, each type of metallic ion is attracted to a different degree. This attraction is measured as the Kd (equilibrium distribution coefficient) of the ion (S-32). It was found that the effect of the Kd was minimized when small volumes (40 ml) were used. Thus each ion is on an equal footing and the amounts of the ions collected from a solution containing a number of ions will accurately reflect the composition of that solution when small volumes are used.

The ion exchange papers used were Reeve-Angel SA-2 which contained up to 50 per cent amberlite IR-120 ion exchange resin. These were chosen because:

-they capture positively charged ions which is the state in which most dissolved metals are found

-they function best at a pH of 2 which is an advantage when working with metallic ions that are subject to hydrolysis

-they have good physical strength and fast flow rate.

In order to make the papers compatible with existing apparatus designed for Millipore filter papers, the ion exchange papers are specially ordered - cut by Reeve-Angel to a 47 millimeter diameter.

The process of activating the ion exchange papers was begun by soaking a number of papers (usually a dozen) in distilled water for several minutes. Then the papers were loaded into an ion exchange tube (Fig. 26). A 40 milliliter volume of 6N HCL was then poured into the tube which then trickled thru the filter. It was collected in a beaker and repoured into the tube. This operation was repeated five times. The same was done to a fresh 40 milliliter volume.

To rid the papers of excess acid, the tube was filled twice with 40 milliliters of distilled water. Next a 40 milliliter volume of saturated NaCl solution was allowed to flow through the papers five times. This was

Table IX

Element	Minimum ug Amount Detectable	Sensitivity Limit For 500 ml Sample (ppm)
Vanadium	48	.096
Chromium	30	.060
Iron	16	.032
Nickel	10	.020
Copper	11	.022
Zinc	12	.024
Arsenic	7	.014
Zirconium	10	.020
Cadmium	12	.024

repeated with fresh volumes of salt solution until the pH of a volume did not change after a pass through the papers.

After activation was completed, the tube was loaded with 200 milliliters of distilled water to wash any remaining salt solution out of the papers. Finally the papers were removed and allowed to dry flat on a hot plate between two glass sheets. Although this is the recommended activation procedure, it was found that the ion exchange papers were excessively brittle due to this procedure.

The ion exchange tube (Fig. 26) consists of a long glass tube approximately 1 3/4 inches in diameter. It ends in a tapered joint upon which a polyethylene cap is located. The ion exchange paper is loaded between the joint and the cap. A large hole in the cap allows water to escape the tube. Although the tube was 19 inches in length, it need only be long enough to hold several hundred milliliters. Due to the mechanical weakness of the ion exchange papers, care should be taken to pour liquids down the side of the tube, instead of directly on the loaded paper.

With this type tube, some problems with solution leaking around the loaded paper developed. In order to combat this, a new tube configuration (Fig. 27) was tried. It consisted of two 1 3/4 inch diameter glass tubes, one 19 inches long and the other 6 inches long. At one end of each of the tubes, the tube widened into a thick lip. A teflon ring with two vinyl O-rings fitted between the two lips. The ion exchange paper was loaded between the ring and the lower lip. The entire apparatus fitted together tightly. The solution could not pass around the loaded paper, but had to flow through it.

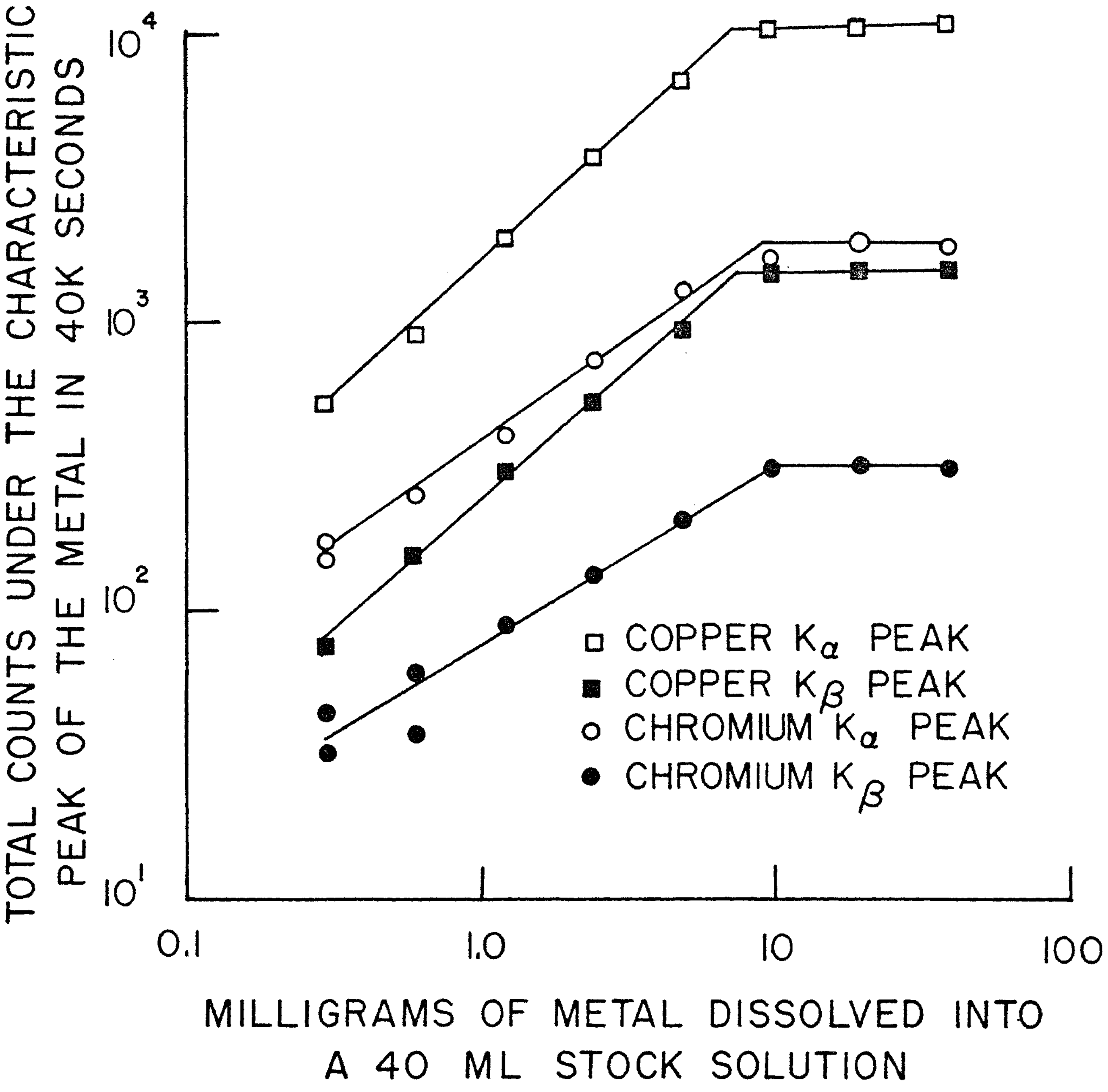


Figure 28. Calibration plots for copper and chromium using ion exchange filter papers.

The determination of the relationship between count rate of X-rays and concentration of metal ions was determined by passing prepared standard solutions of known concentration through the filter paper. The elements in the stock solutions were picked on the basis of being commonly found in suspended solids in the local river. These included iron, copper, chromium, cadmium, and lead.

The technique used to make a standard solution was to pick a water soluble salt of the metal in question, determine the amount needed to create a gram of metal ions per liter (1000 ppm), and dissolve it in a liter of distilled water. Via dilution, solutions were made with concentrations from 0.3 milligrams/liter to 38.4 milligrams/liter. These were passed through the ion exchange papers and analyzed with X-ray fluorescence. From this calibration, curves were made (see Fig. 28 for copper and chromium). Some problems developed with the iron solutions because iron easily precipitates out, even when the standard solution was acidic. Thus, the concentration of metallic ions which can be captured by the ion exchange paper is never constant and a calibration curve is difficult to construct. No iron salt that was tried proved to form a sufficiently stable solution to allow a calibration curve to be constructed. Because of the difficulty in preparing an iron standard, other metals were tried.

A working volume of 40 ml proved to be the best. Each ion possesses an equilibrium distribution coefficient which determines the degree to which it is attracted by the ion exchange resin. In order to insure that all ions are equally taken out of solution and thus that experimental measurements accurately reflect the concentrations of the ions present in solution, a solution volume of 40 ml or lower is best. That this is so is seen from the following equation. Fraction of ion exchanged = $[(Kd)(g)]/[(Kd)(g) + W]$ where:

Kd = equilibrium distribution coefficient of the ion

g = mass of ion exchange resin

W = volume of water containing the ion (expressed as mass).

Since large volume solutions allows more sensitivity, 40 ml was chosen for the working volume.

If the solution to be studied for ionic content is passed through the ion exchange paper, a number of times, more of the ions present in the solution will be captured than would have if the solution was passed through the paper only once. Since larger numbers of ions captured allows greater sensitivity, it is advantageous to collect as many as possible. It was found that after three passes, the paper and solution are in equilibrium and no more ions will be captured by additional passes. Nevertheless, 7 passes were made to insure all possible ions were collected.

G. Results of Survey of Great Miami River

Table X shows the results of the study of several outfalls on the Great Miami River. Each different location was from the outfall of a major industry. When metals are not listed an upper limit on their presence is given by the sensitivity limit listed on Table IX. Some typical spectra from which the above results were determined are shown in Figs. 29-34.

Table X

The values shown in this table are in parts per million (ppm) of the original water sample. The amount sampled varied from 200-500 ml. The nine sampling locations were outfalls on the Great Miami River from industries in the Dayton, Ohio area. All dates shown are between October, 1970 and March, 1971. When values are not shown for particular elements or when elements are not listed, an upper limit of their presence can be found from the sensitivity limits shown in Table IX. The errors on the numbers shown are 10% for Fe, Zn and Cu, 12% for Sr, Zr, Cn and Cd. Ca and Ti were at the very end of the efficiency curve and can be considered as lower limits with an error of no more than 30%

Sampling Location I

Date	Ca	Fe	Zn	Other
10/8		0.99		
10/8		1.92		
10/8		0.67	0.16	
9/30	0.62	0.61	0.07	
10/22	0.25	0.23	0.03	
10/22	0.27	0.31	0.02	
10/24	0.28	0.38	0.05	
10/24	0.50	0.57	0.02	0.05 Ti
10/24	0.53	0.46	0.03	
10/31	0.53	0.47	0.39	
10/31	0.44	0.43	0.04	
10/31	0.44	0.41	0.05	0.09 Cu
10/31	0.38	0.42	0.04	
11/7	0.25	0.32		
11/7	0.86	0.39	0.03	
11/14	0.43	0.32	0.03	
11/14	0.50	0.29	0.03	
11/14	0.28	0.33	0.03	
11/19	0.28	0.33	0.21	
11/19	0.14	0.27	0.04	
11/19		0.13		
11/21	0.36	0.55		
11/21	0.32	0.46		
11/21	0.28	0.49	0.03	
11/21	0.22	0.30	0.02	
1/26	0.24	0.14		

Sampling Location II

Date	Ca	Ti	Fe	Zn	Sr	Other
10/31			0.34	0.03		
11/7	0.68		1.54	0.32	0.13	
11/7	0.22	0.24	8.68	0.37		
11/12			3.89	0.25		
11/12			0.23			
11/14	0.40		1.70	0.70	0.07	
11/19			0.52	0.03		
11/21			0.13			
11/21	0.28		2.33	12.57	0.13	
12/3	0.17		3.20	0.19		
12/10	0.37	0.15	7.49	0.26		
12/12			1.24	0.04		
12/12		0.28	1.06	0.03	0.02	
12/5		0.28	2.64	0.03	0.26	0.60 Zr
12/22			32.54	1.19	0.29	0.23 Zr
1/14	0.30		0.72			
1/14	0.28		0.99	0.03		
12/22	0.99		0.42	8.60	0.10	
1/18		0.37	1.37		0.04	
1/26			0.13			
2/3		0.23	1.09	0.03	0.03	
2/3			0.89	0.06		
2/25	0.34	0.20	3.17	0.18		
3/25		0.19	1.24		0.08	

Sampling Location III

Date	Fe	Zn	Ca
10/22	0.70		0.09
10/29	1.31	0.01	
11/7	0.62		

Sampling Location IV

Date	Ti	Ca	Fe
11/23	5.35	0.18	0.18

Sampling Location V

Date	Fe
11/19	0.32

Sampling Location VI

Date	Ca	Fe	Cu	Zn	Other
10/22	0.30	0.62	0.48	0.67	0.07 Cd
11/7		2.61	0.06		0.35 Cr
11/28		0.22			
12/10	0.52	0.89	0.03	0.61	
12/22	0.32	0.67		0.33	
1/9	0.10	1.16	0.11	0.02	0.02 Cr.
1/26	0.82	0.68		0.29	0.04 Cr.
2/25	0.81	0.52		0.22	

Sampling Location VII

Date	Ca	Fe	Cu	Zn	Other
10/22	0.14	0.05			
10/24	0.21	0.45	0.04	0.04	
10/29		0.40	0.02	0.03	
10/29	0.47	0.40	0.04	0.06	0.30 Ti
10/31		0.13	0.03	0.03	
11/7		0.21			0.11 Ti 0.09 Cr
1/9		0.79		0.02	

Sampling Location VIII

Date	Ca	Fe	Zn	Sr
10/31	4.96	0.03		0.29
10/31	0.59	0.92	6.2	0.19

Sampling Location IX

Date	Ca	Fe	Zn	Sr	Other
10/31	0.59	0.92	6.2	0.19	
11/7	0.12	1.55	0.29	0.11	
11/19	1.06	0.54	2.83	0.17	
11/14	1.63	2.76	3.85	0.68	
11/28	0.28	1.04	0.14	0.07	
11/28		0.07			
12/3	0.92	0.73	5.82	0.26	
12/10	0.74	1.17	1.85	0.09	
12/12	0.05	2.84	0.07	0.06	0.03 Cu
12/28		0.50			
1/9	0.91	2.88	0.42	0.10	
1/14		0.89	10.9	0.11	
1/18	0.75	0.77	5.42		
1/26	1.32	0.56	2.54	0.17	
2/3	0.35	0.86	12.71	0.22	
2/25	0.99	0.95	4.56	0.11	
3/18		0.60	3.48	0.10	

Snow From Sherman Hall (University of Dayton)

Date	Ca	Fe	Cu	Zn	Other
1/18	0.61	3.33	0.21	0.06	0.64 Ti
1/28	1.6	2.62			0.06 Sr 0.24 Ti
1/29	0.41	0.29			
2/8	0.10	0.07	0.04	0.09	

Tap Water From Sherman Hall (University of Dayton)

Date	Fe	Zn
11/21	0.16	0.65
2/8	0.10	0.14

Steele Dam

Date	Ca	Fe	Cu	Zn
1/18	0.14	7.21	0.02	
1/26		1.74	0.08	0.05

Holes Creek

Date	Fe	Cu	Zn	Ca
10/31	0.76	0.03	0.05	0.63

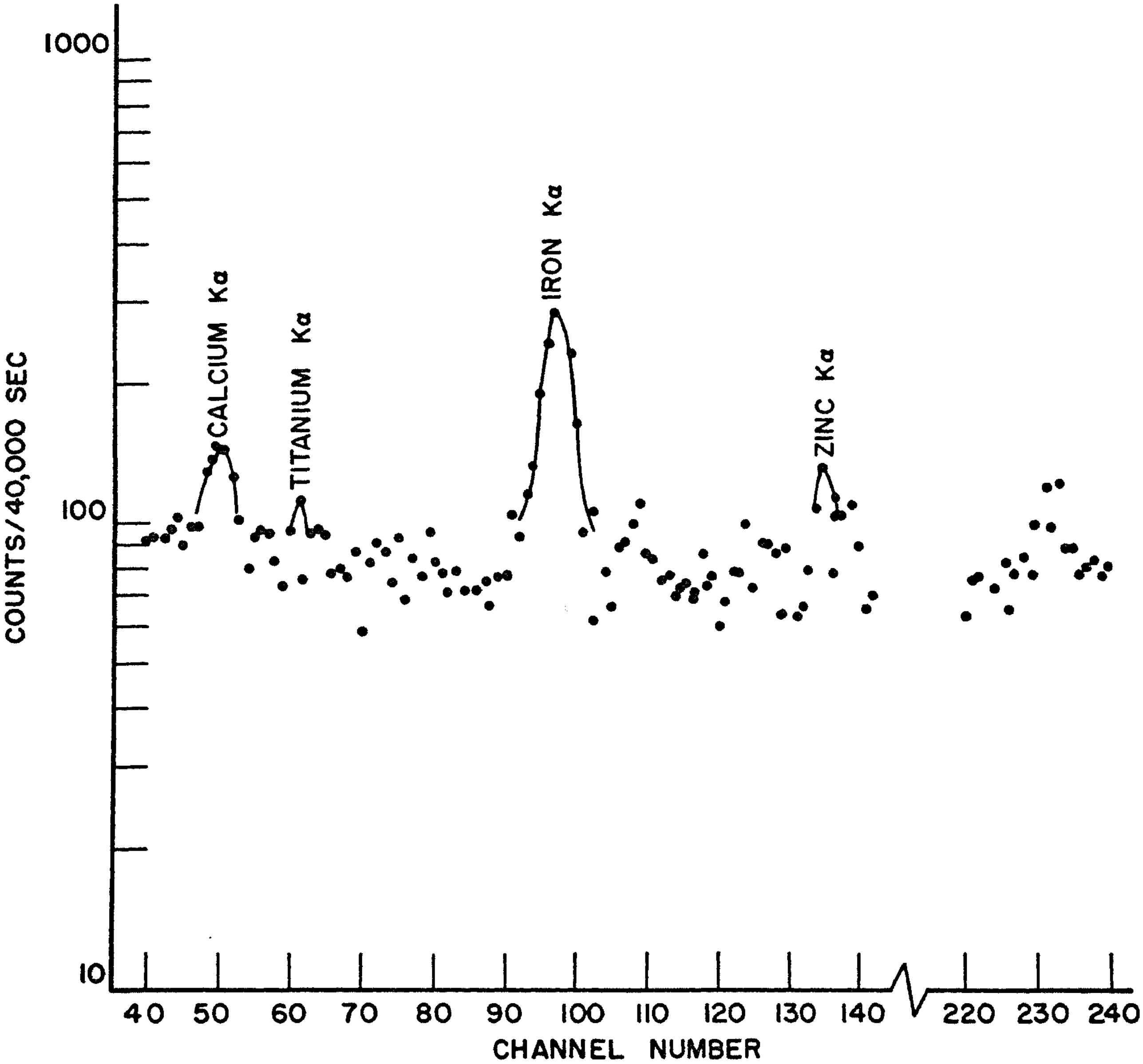


Figure 29. X-ray fluorescence spectra of water sample from location I taken 11/19.

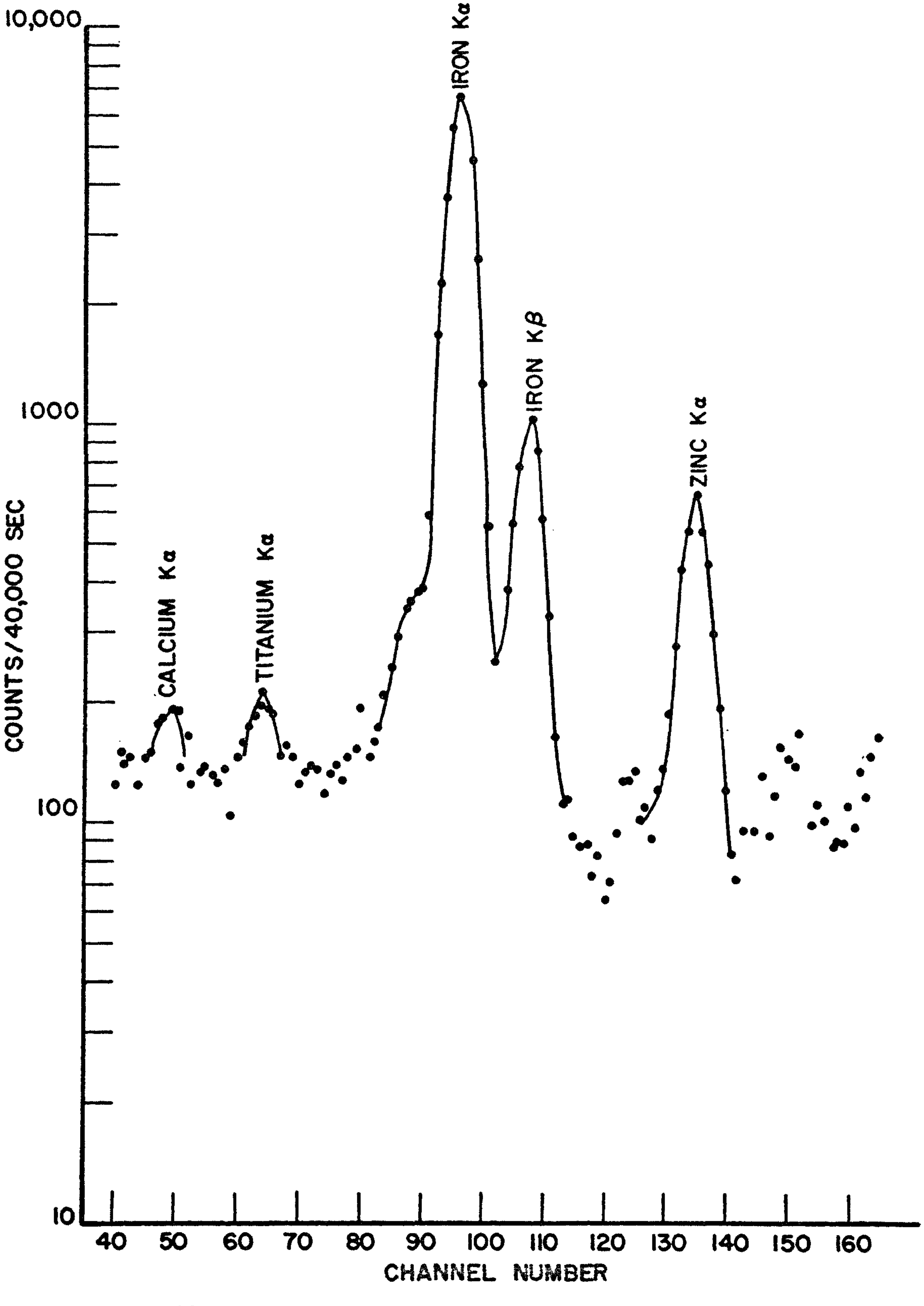


Figure 30. X-ray fluorescence spectra of water sample from location II taken 11/7.

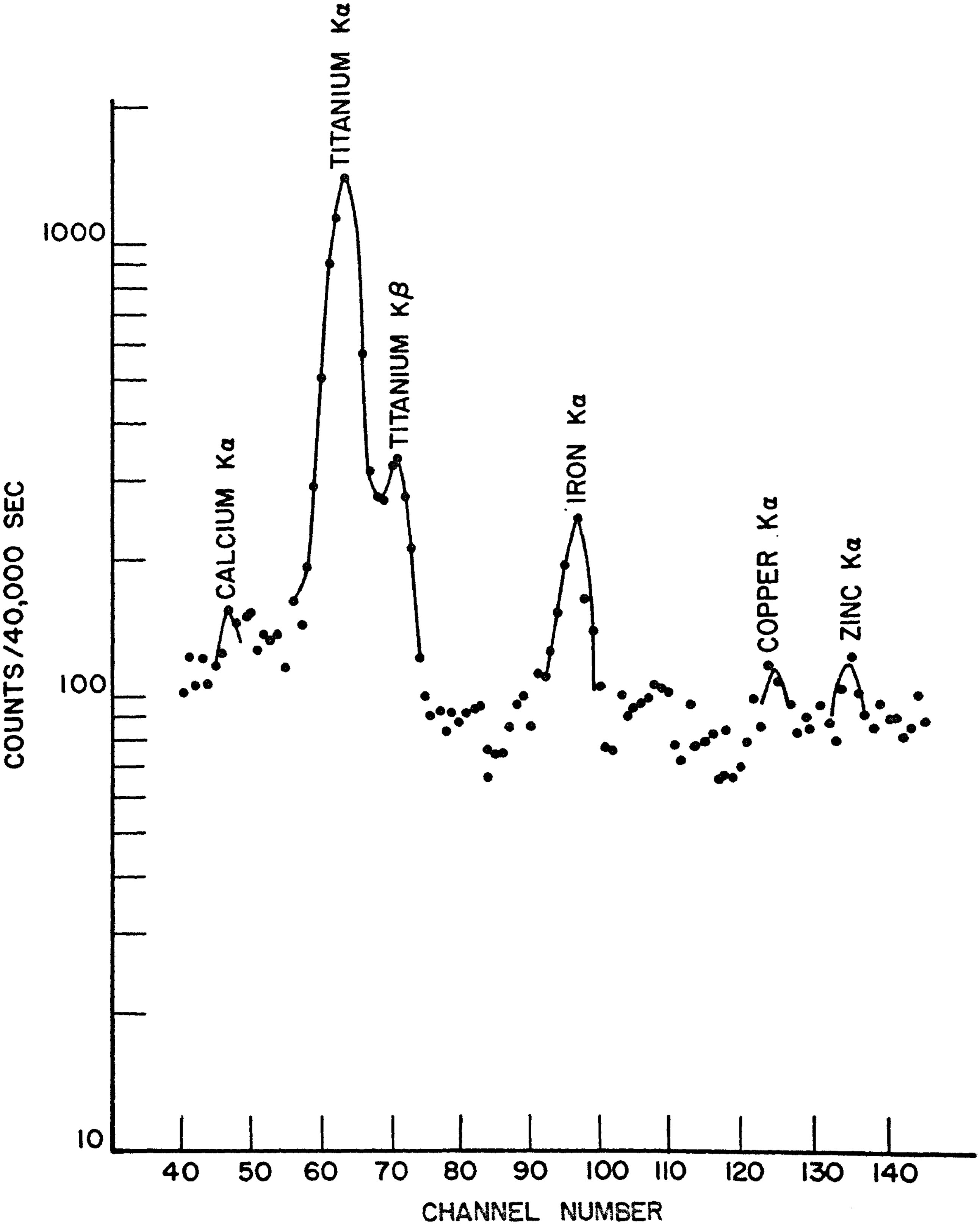


Figure 31. X-ray fluorescence spectra of water sample from location IV taken 11/23.

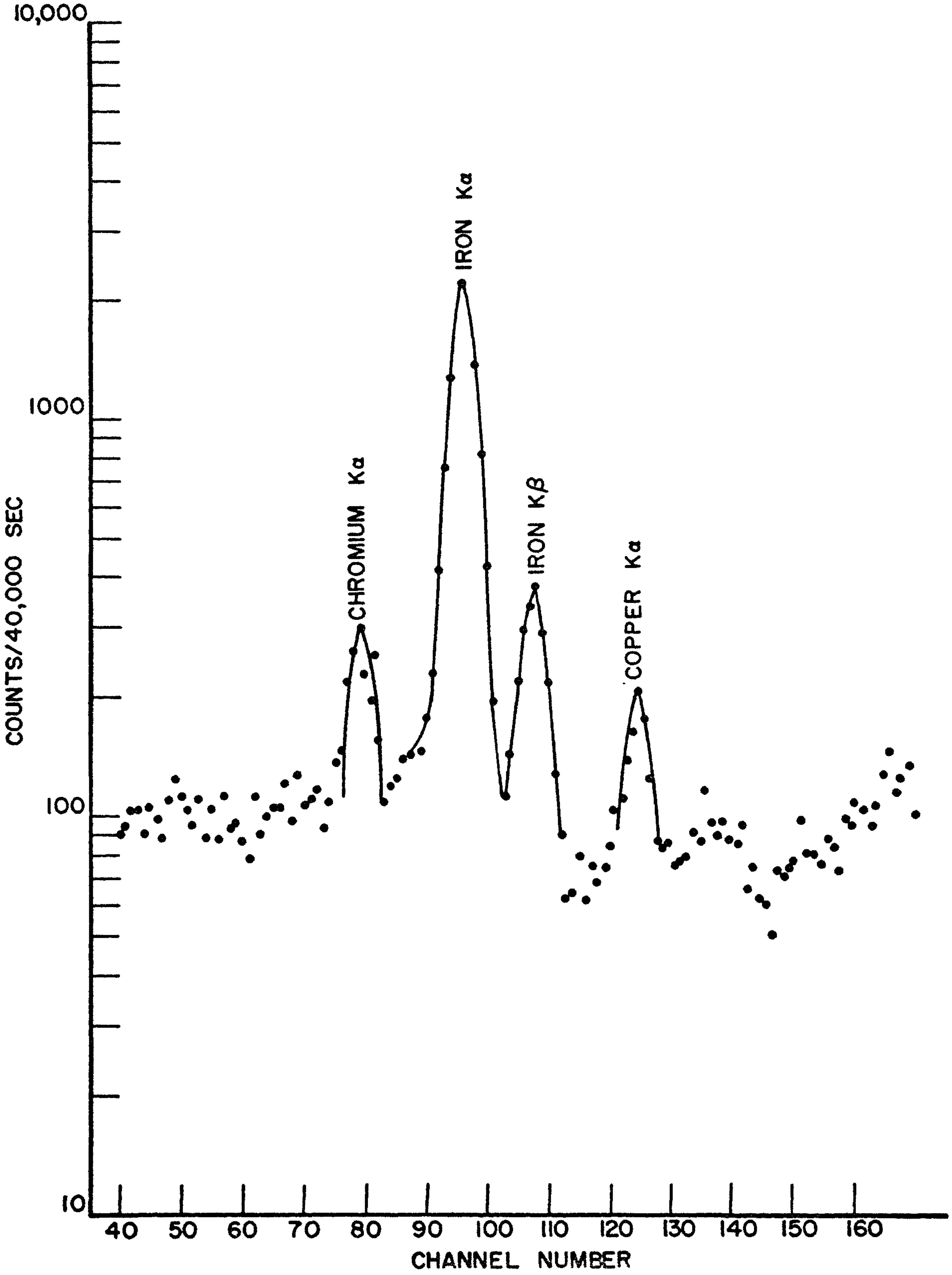


Figure 32. X-ray fluorescence spectra of water sample from location VI taken 11/7.

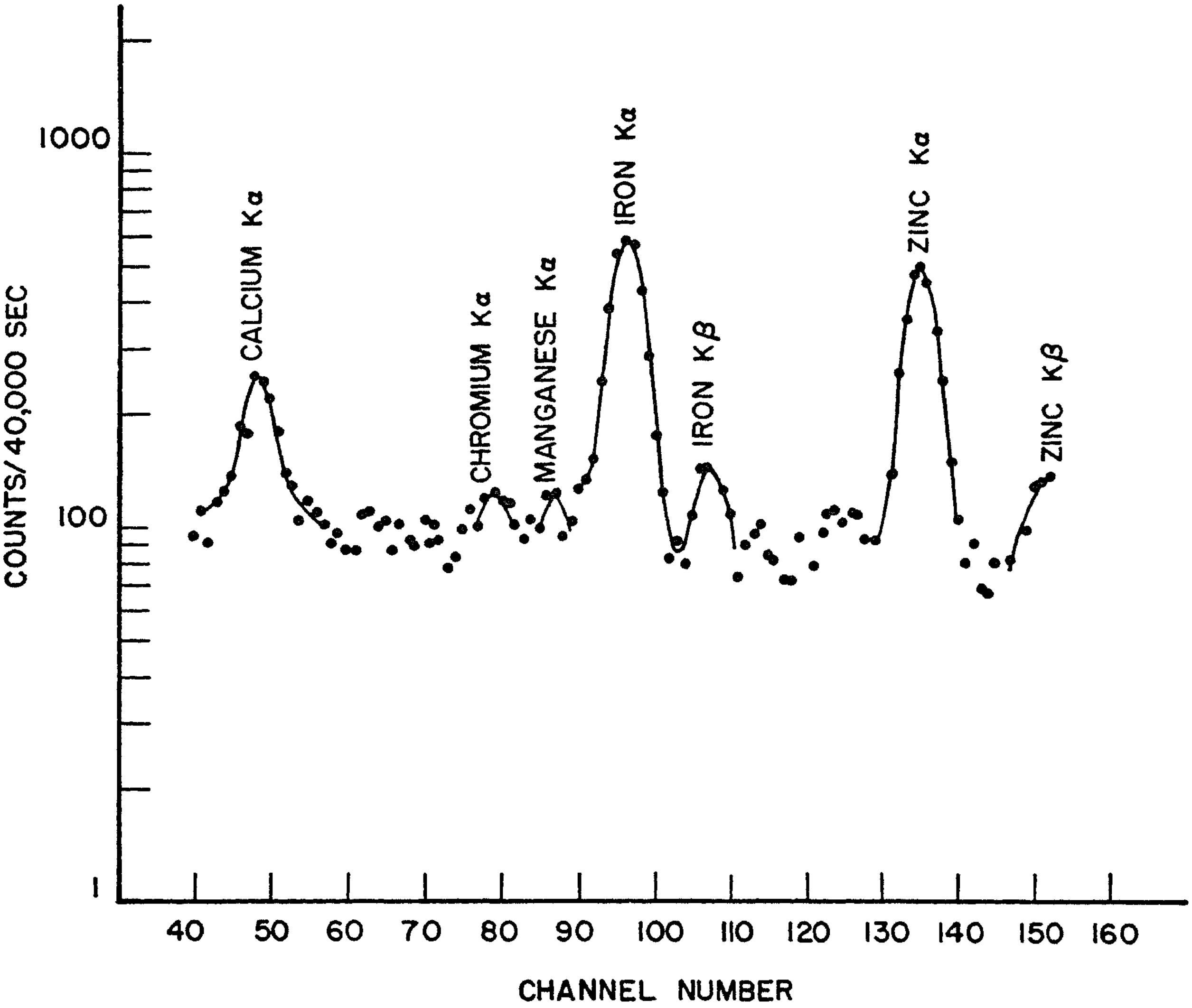


Figure 33. X-ray fluorescence spectra of water sample from location VI taken 1/26.

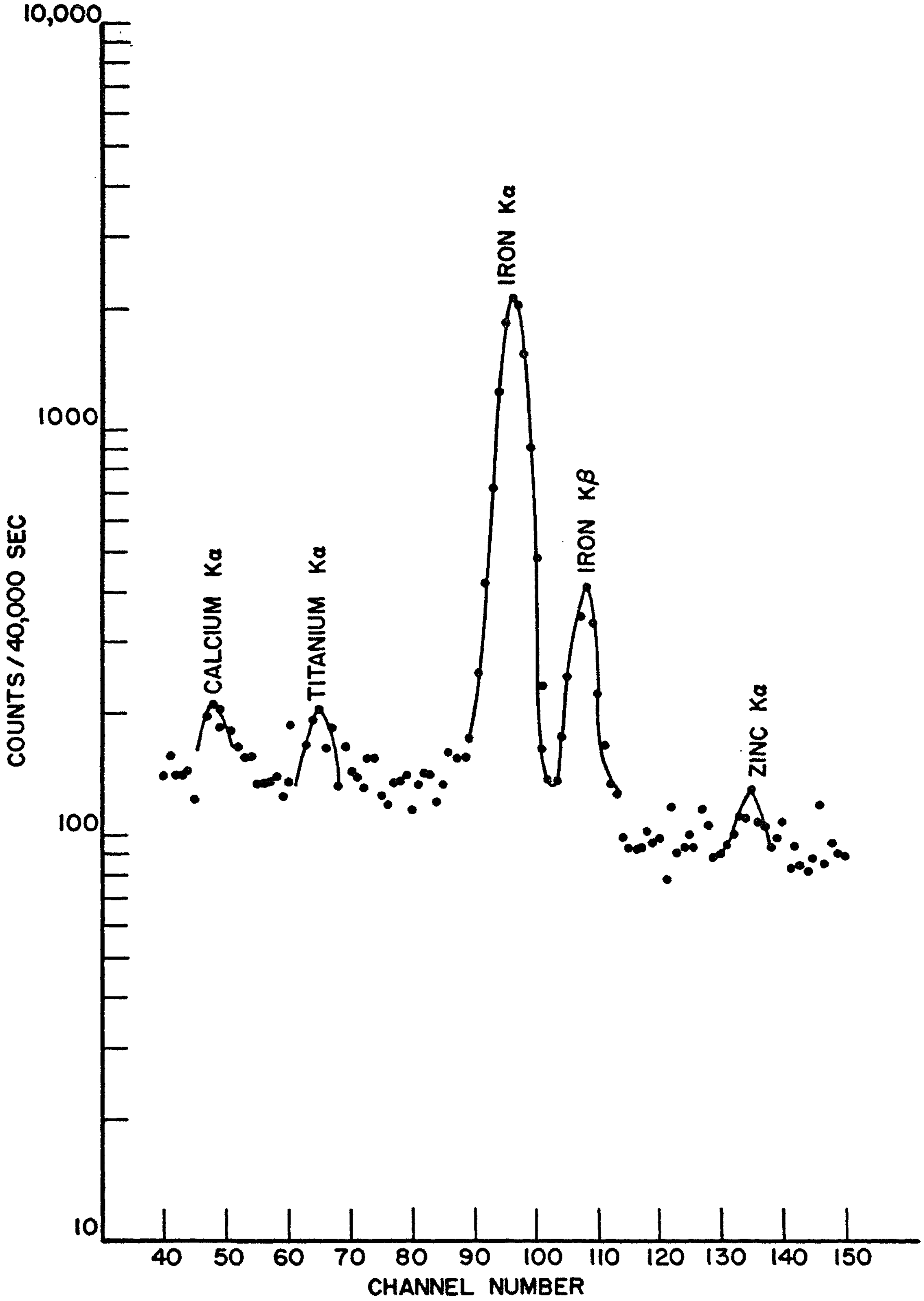


Figure 34. X-ray fluorescence of snow sample collected on top of Sherman Hall, University of Dayton, 1/28.

Chapter V Discussion and Conclusion

As shown by this report, the X-ray fluorescence method is capable of determining in water samples the trace metals between Ti and Cs in the periodic table to a sensitivity limit of 20-30 ppb. This demonstrates that XRF is a valuable analytical tool in the investigation of trace metals in water resources. The problem areas with this technique are primarily in the sample preparation stage. Matrix effects provide some difficulties while the most important need which emerged in this work concerning the analysis of trace metals in water resources was the determination of what chemical and/or physical form the metal occurs. Techniques will be developed to determine these properties.

It appears that some of the metals are in the suspended state (size greater than 0.45 microns) and the rest are either ionized or attached to colloidal particles. It seems important to investigate these properties and work has been started in this direction by using ion exchange filter papers to collect the ionized metals. After filtration with 0.45 micron pore size filters and ion exchange filter papers, the water sample can be evaporated to test for the presence of metals in colloidal form.

For the future, it is planned to conduct studies concerning the matrix effects. Standardized samples will be prepared with various mixes of metals and with various amounts of low Z materials, to study both the enhancement and absorption effects as they apply to concentration determinations of trace metals. Since heavy metals (mainly lead and mercury) are becoming more important, an efficiency curve will be determined for L X-rays.

The use of ion-exchange filter papers allows some studies of the charge state of the metals to be made. It is hoped to study the charged state of both ionized metal, and those attached to colloids by this method.

Acknowledgements

We wish to thank Dr. Donald Washington and the Water Resources Center at Ohio State University, Columbus, Ohio, for their financial assistance, advice and consideration in this project. We wish also to acknowledge financial assistance from the University of Dayton Research Council, the Research Corporation and the National Science Foundation.

We wish also to thank Mr. Richard Grant for his advice and help in preparing glassware, Mr. B. A. Placke for help in fabricating various parts in the shop, Miss C. Comer for help in preparing the drawings, and Dr. J. J. Kepes for his continuous encouragement throughout this project and for proofreading this manuscript.

References

A-1 Aiyar, A. S. and Sreenivasan, A., Proc. Soc. Biol. Med. 107, 914 (1961).

A-2 Amdur, M. O. and Underhill, D., Arch. Environ. Health 16, 460 (1968).

A-3 A. S. T. M. Symposium on Fluorescent X-ray Spectrographic Analysis, A. S. T. M. Special Technical Publication No. 157, Philadelphia, 1954, pg. 9.

A-4 Adler, I., "X-ray Emission Spectrography in Geology", Elsevier Publishing Co., New York, 1966.

A-5 Alley, B. J. and Myers, R. H., Norelco Reporter, 15, 87 (1968).

A-6 American Chemical Society, "Cleaning Our Environment; the Chemical Basis for Action", Washington, D. C., 1969, and Supplement to the above, 1971.

A-7 Amersham/Searle, 2636 S. Clearbrook Dr., Arlington Heights., Ill. 60005.

B-1 Bonser, G. M., Faulds, J. S. and Stewart, M. S., Am. J. Clin. Pathol. 25, 126 (1955).

B-2 Buechley, R. W., Am. J. Pub. Health 53, 1229 (1963).

B-3 Bowman, H. R., Hyde, E. K., Thompson, S. G. and Jored, R. C., Science 151 562 (1966).

B-4 Bunch, D. and Richard, P., Phys. Rev. Letts. 25, 983 (1970).

B-5 Brown, G. A., Nelson, D. A. and Ritzert, W., Am. Laboratory, March, 1971, pg. 15.

B-6 Berry, P. F., 16th National Symposium, Analysis Instrumentation Division, Instrument Society of America,,Pittsburgh, Pa., 1970.

B-7 Bergmann, S. G., Ehrhardt, C. H., Granotelli, L. and Janik, J. L., Anal. Chem. 39, 1258 (1967).

B-8 Bergmann, J. G., Ehrhardt, C. H., Granotelli, L. and Jonik, S. L., Anal. Chem. 39, 1331 (1967).

B-9 Blasius, M. B. and Cothern, C. R., Bull. Am. Phys. Soc., to be published, from Ohio Section APS Meeting, Dayton, Ohio, May, 1971.

C-1 Christie, H., MacKay, R. J. and Fisher, A. M., Am. Ind. Hug. Assoc. J. 24, 47 (1963).

C-2 Curran, G. L., J. Biol. Chem. 210, 765 (1954).

C-3 Carroll, R. E., J. Am. Med. Assoc. 198, 177 (1966).

C-4 Cahill, T. A., Commerville, R., Flocchini, R., Brady, F. P., and Peek, N. F., Bull. Am. Phys. Soc. 16, 434 (1971).

C-5 Campbell, W. J., Green, T. E. and Law, S. L., Am. Laboratory, 28, June, 1970.

C-6 Campbell, W. J., Spano, E. F., and Green, T. E., Anal. Chem. 38, 987 (1969).

C-7 Chamberlain, B. R., and Leech, R. J., Talanta, 14, 597 (1967).

C-8 Californium - 252, "Its use and Market Potential and Californium - 252 Progress", Numbers 1, 2, 3, 4, 5, and 6, United States Atomic Energy Commission, 1969-1971.

D-1 Davis, G. K., Proceedings of the Third Annual Conference on Trace Substances in Environmental Health, Columbia, Mo. 1969, pg. 135.

D-2 Duncan, G. D., Gray, L. F., and Daniel, L. S., Proc. Soc. Expl. Biol. Med. 83, 625 (1953).

D-3 G. Dugan, Private Communication

D-4 Davis, E. N., and Van Nordstrent, R. S., Anal. Chem. 26, 973 (1954).

D-5 Dittrich, T. R. and Cothern, C. R., Bull. Am. Phys. Soc. 15, 846 (1970).

D-6 Dittrich, T. R. and Cothern, C. R., J. Air Pollution Control, to be published.

E-1 Ewan, G. T. and Tavendale, A. J., Can. J. Phys. 42, 2286 (1964).

E-2 Elad, E. and Nakamura, M., Nucl. Instr. and Met. 41, 161 (1966).

F-1 Freeman, H. E., J. Am. Med. Assoc. 119, 1016 (1942).

F-2 Ferm, V. H. and Carpenter, S. J., J. Reprod. Fert. 19, 199 (1968).

F-3 Fox, M. R. S. and Fry, B. E., Science 169, 989 (1970).

F-4 Friedman, H. and Birks, L. S., Rev. Sci. Instr., 19, 323 (1948).

F-5 Fink, R. W., Jopson, R. C., Mark, H., and Swift, C. D., Rev. Mod. Phys. 38, 513 (1966).

F-6 Felten, E. J., Fonkuchen, I., and Stergman, S., Anal. Chem. 31, 1771 (1959).

G-1 Gray, L. F., and Ellis, G. H., J. Natr. 40, 441 (1950).

G-2 Goulding, F. S., UCRL-11302, unpublished report from Lawrence Radiation Laboratory, University of California, Berkeley, Calif., 1964.

G-3 Gilmore, F. R., "Graphs of X-ray Absorption Coefficients for Fourteen Substances", Report no. RM-2367 AEC, The Rand Corporation, 1959.

G-4 Goulding, F. S., Nuc. Instr. & Met. 43, 1 (1966).

G-5 Giaugue, R. D., UCRL-18292, Lawrence Radiation Laboratory, University of California, 1968.

G-6 Gorcia, S. D., Phys. Rev. 5A, 1402 (1970).

G-7 Grubb, W. T. and Zemary, P. D., Nature 176, 221 (1955).

G-8 Gleason, G. I., Private Communication

H-1 Hueper, W. C. and Payne, Am. Ind. Hug. Assoc. J. 21, 530 (1960).

H-2 Hill, W. H. and Worden, F. X., Am. Ind. Hug. Assoc. J. 23, 186 (1962).

H-3 Hueper, W. C., J. Nat. Cancer Inst. 16, 447 (1955) and Hueper, W. C., AMA Arch. Pathol. 65, 600 (1958).

H-4 Hygiene Guide Series, Am. Ind. Hug. Assoc. J., Nov.-Dec. 1964, pg. 610.

H-5 Von Hevesy, G., "Chemical Analysis by X-rays and Its Applications", University Press, Cornell, 1932.

H-6 Von Hevesy, G. and Covter, D., Nature 79, 111 (1923).

H-7 Hollander, J. M., Nuc. Instr. & Met. 43, 65 (1966).

H-8 Hubbard, G. L. and Green, T. E., Anal. Chem. 38, 428 (1966).

J-1 Johansson, T. B., Akselsson, R. and Johansson, S. A. E., Nuc. Instr. & Met. 84, 141 (1970).

J-2 Jenkins, R. and De Vries, J. L., "Practical X-ray Spectrometry", Phillips Technical Library, Springer-Verlag, New York, 1967.

K-1 Kleinfeld, M., Messite, S., Shapire, J., Kooyman, O. and Levin, E., Arch. Environ. Health 16, 392 (1968).

K-2 Kincaid, Stanley, E. L., Beckworth, C. H. and Sunderman, F. W., Am. J. Clin. Pathol. 26, 107 (1956).

K-3 Konisawa, M. and Schroeder, H. A., Cancer Res. 27, 1192 (1967).

K-4 Kanisawa, M., and Schroeder, H. A., Cancer Res. 29, 892 (1969).

K-5 Kevex Corporation, "Analytical Methods for Energy Dispersive X-ray Spectrometry", unpublished report, 898 Mahler Rd., Burlingame, Calif., 1969.

K-6 Kolthoff, I. M. and Elving, P. S., "Treatise on Analytical Chemistry", Part I, Volume 5, Interscience Publishers, 1959.

K-7 Kevex Corp., 898 Mahler Rd., Burlingame, Calif.

K-8 Krushaar, J. J., Ristinen, R. A., Rudolph, H. and Smyth, W. R., Bull. Am. Phys. Soc. 16, 545 (1971).

K-9 Kopp, J. F. and Kroner, R. C., "A comparison of trace elements in natural waters, dissolved versus suspended", presented at the 18th Annual Mid-American Symposium on Spectroscopy, Chicago, Ill., 1967.

K-10 Karttunen, J. O. and Henderson, J. S., Anal. Chem. 37, 307 (1965).

L-1 Luke, C. L., Analytica Chema Acta 41, 237 (1968).

L-2 Laurer, G. R., Kneip, T. J. and Albert, R. E., Science 172, 466 (1971).

L-3 Luke, C. L., Analytica Chemica Acta 43, 245 (1968); 45, 377 (1969).

L-4 Luke, C. L., Anal. Chem. 36, 318 (1964).

L-5 Liebhafsky, H. A., Pfeiffer, H. C., Winslow, F. H. and Zemoy, D. D., "X-ray Absorption and Emission in Analytical Chemistry", John Wiley, New York, 1960.

M-1 Mountain, J. T., Stockell, F. R., Jr., and Stokinger, H. E., Proc. Soc. Exp. Biol. Med. 92, 582 (1955).

M-2 Morgan, J. G., Brit. S. Industr. Med. 15, 224 (1958).

M-3 Milner, S. E., Arch. Environ. Health 18, 7 (1960).

M-4 Moseley, H. H. J., Phil. Mag. 26, 1013 (1913); Phil. Mag. 27, 703 (1914).

M-5 Meyer, J. W., Nuc. Instr. & Met. 43, 55 (1966).

M-6 Mitchell, B. J., Anal. Chem. 32, 1652 (1960).

M-7 Mitchell, B. J., Anal. Chem. 30, 1894 (1958).

M-7 McCrone, W. C., American Laboratory 3, No. 4, 8 (1971).

N-1 Northern Scientific, Inc., 2551 West Beltline, Middletown, Wisconsin.

N-2 National Bureau of Standards, Office of Standard Reference Materials, Washington, D. C., 20234

O-1 Oberleas, D. and Prasad, A. S., unpublished report, 1969, Dept. of Medicine, Wayne State University.

O-2 Ortec, Inc., 100 Midland Rd., Oak Ridge, Tenn.

O-3 Ortec Laboratory Manual-A, Ortec, Inc., 100 Midland Rd., Oak Ridge, Tenn.

P-1 Perry, H. M., Jr., Teitelbaum, S. and Schwartz, P. L., Fed. Proc. 14 113 (1955).

P-2 Pfitzer, Emil, Dept. of Environmental Health, College of Medicine, University of Cincinnati, Private Communication.

P-3 Pfeiffer, H. G. and Zemany, P. D., Nature 174, 397 (1954).

R-1 Rose, U. C., unpublished report, "Analysis of trace elements in water", University of Rhode Island, 1969.

R-2 Reeve-Angel Co., 9 Bridgewell Place, Clifton, New Jersey.

S-1 Schroeder, H. A., J. Chron. Dis. _18_, 217 (1965).

S-2 Schroeder, H. A., Virton, W. H. and Balassa, J. J., J. Nutrition _80_, 39 (1963).

S-3 Snyder, F. and Cornatzer, W. E., Nature _182_, 462 (1958).

S-4 Schroeder, H. A., Balassa, J. J. and Tipton, I. H., J. Chron. Dis. _16_, 1047 (1963).

S-5 Schroeder, H. A., Balassa, J. J. and Tipton, I. H., J. Chron. Dis. _15_, 941 (1961).

S-6 Shelley, W. B., J. Am. Med. Assoc. _189_, 170 (1964).

S-7 Schroeder, H. A., Balassa, J. J. and Tipton, I. H., J. Chron. Dis. _15_, 51 (1961).

S-8 Sunderman, F. W. and Sunderman, F. W., Jr., Am. J. Clin. Pathol. _35_, 203 (1961).

S-9 Sunderman, F. W., Ronge, C. S., Sunderman, F. W., Jr., Donelly, A. S. and Lucszyn, G. W., Am. J. Clin. Pathol. _36_, 477 (1961).

S-10 Sunderman, F. W., Am. J. Clin. Pathol. _39_, 549 (1963).

S-11 Sunderman, F. W., Nomoto, S. and Nechay, M., Proc. of Fourth Annual Conf. on Trace Substances in Environment Health, pg. 352, Columbia, Mo. 1970.

S-12 Scheinberg, I. H., Proc. Third Annual Conf. on Trace Substances in Environmental Health, pg. 79, Columbia, Mo. 1969.

S-13 Sadasivan, V., Biochem. J. _48_, 527 (1951); _49_, 527 (1951); _52_, 452 (1952).

S-14 Stewart, A. K. and Macgee, A. C., J. Jutrition _82_, 287 (1964).

S-15 Schroeder, H. A. and Balassa, J. J., J. Nutrition _92_, 245 (1967).

S-16 Schroeder, H. A., Kanisawa, M. Frost, D. V. and Mitchener, M., J. Nutrition _96_, 37 (1968).

S-17 Schroeder, H. A. and Balassa, J. J., J. Chron. Dis. _19_, 85 (1966).

S-18 Schroeder, H. A., Mitchener, M., Balassa, J. J., Kanisawa, M. and Nason, A. P., J. Nutrition 95, 95 (1968).

S-19 Schroeder, H. A. and Balassa, J. J., J. Chron. Dis. 19, 573 (1966).

S-20 Schroeder, H. A., Mitchener, M. and Nason, A. P., J. Nutrition 100, 59 (1970).

S-21 Schroeder, H. A., Nason, A. P., Prior, R. E., Reed, J. B., and Haessler, W. T., Am. J. Physio. 214, 469 (1968).

S-22 Schroeder, H. A., Baker, J. T., Hansen, N. M., Jr., and Wise, R. A., Arch. Environ. Health 21, 609 (1970).

S-23 Schroeder, H. A. and Balassa, J. J., J. Chron. Dis. 14, 236 (1961).

S-24 Schroeder, H. A., Am. J. Physio. 207, 62 (1964).

S-25 Siegbahn, K., ed. "Alpha, Beta and Gamma Ray Spectroscopy", North-Holland Publishing Co., 1966.

S-26 Singh, B. and Al Dargazelli, S. S., Phys. Rev. 3C, 364 (1971).

S-27 Spano, E. F. and Green, T. E., Anal. Chem. 38, 1341 (1966).

S-28 Sherma, J., Anal. Chem. 36, 690 (1964).

S-29 Spano, E. F., Green, T. E. and Campbell, W. J., U. S. Dept. of the Interior, Bureau of Mines, R. I., 6565 (1964).

S-30 Sherman, J., Spectrochimica Acta 7, 283 (1955).

S-31 Solazzi, M. J., Am. Laboratory, pg. 69, June, 1971.

S-32 Samuelson, V., "Ion Exchange Separations in Analytical Chemistry", Wiley, New York, 1963.

S-33 Skougstad, M. W. and Scarbro, G. F., Jr., Environ. Sci. & Tech. 2, 298 (1968).

S-34 The Staplex Company, 777 Fifth Ave., New York, New York.

W-1 Warnick, S. L. and Bell, H. L., J. Water Pollution Control Fed. 41, 280 (1969).

W-2 Wilson, H. N., "An Approach to Chemical Analysis", Pergamon Press, New York, 1966.

W-3 Woldseth, R., Porter, D. E. and Frankel, F. S., Ind. Research 46, Feb., 1971.

W-4 Wright, R. S., Kerkhoff, S. J. and Cothern, C. R., Bull. Am. Phys. Soc., to be published, from Ohio Section APS Meeting, Dayton, Ohio, May, 1971.

Y-1 Yamamoto, S., USNRDL-TR-68-77, U. S. Naval Radiological Defense Laboratory, San Francisco, Calif., 1968.

Z-1 Zen, Z. C. and Berg, B. A., Arch. Environ. Health, 14, 709 (1957).

Z-2 Zemany, P. D., Pfeiffer, H. G. and Liebhafsky, H. A., Anal. Chem. 31 1776 (1959).

Determination of Trace Metal Pollutants in Water Resources and Stream Sediments

Office of Water Resources Research
Department of Interior
Project No. 398X

This Final Report Covers Work Done Between
July 1, 1971 and June 30, 1972

C. R. Cothern
Physics Department
University of Dayton
Dayton, Ohio 45409

Table of Contents

Personnel Involved in this Project

Principal Investigator

- C. R. Cothern, Ph. D.

Student Research Assistants

- M. B. Blasius
- C. D. Brown
- C. M. Kessler
- J. R. Millette
- T. P. Schmit
- R. S. Wright

Student Assistants

- J. Holden
- H. Manuel
- R. Moehler
- J. Parlette

Research Consultants

- J. A. Deye, Ph. D.
- J. Walker, Jr., M. S.

Figures

Tables

ABSTRACT

The computer program for analysing the X-ray fluorescent spectra qualitatively and quantitatively is described. The effects of absorption and enhancement are analyzed. Absorption is shown in general to be a negligible effect while the matrix effect known as the enhacement effect is examined in some preliminary studies. A study of sediments from the Great Miami River in Dayton, Ohio yields results that are similar to normal geological values for trace metals indicating a low level of pollution in the river.

The present report is supplemental to last years (OWRR Project Number A-019-Ohio) and together the two reports constitute a final report for the period July 1, 1970 to June 30, 1972.

I. INTRODUCTION

A. Some Recent Developments in X-Ray Fluorescence

A number of developments have occurred in the field of trace metal determinations in environmental samples during the past year.(1) One of these developments concerns the type of excitation source used. The inconvenience of radioactive sources in terms of their radiation hazard has led to the development of X-ray tubes of both low and high power ratings for use in exciting the X-rays. These X-ray tubes give rise to better sensitivities than those produced by radioactive sources but suffer from not being portable. Portable solid state detector systems have been developed.(2)

Much controversy has developed concerning the sensitivities achievable with the different types of excitation. The ionization cross section curves for any kind of particle or photon excitation approach a maximum value of about 10^6 Barns/atom(1) at some incident quantum energy and then decrease slowly; for electrons and gamma rays the maximum is at tens of kilovolts, for protons a few MeV, and for heavy ions a few tens of MeV. However in comparing the sensitivities obtainable in practical circumstances, the sensitivity achievable with a radioactive source (25 millicuries) is about an order of magnitude worse than that achievable with a X-ray tube whose characteristics are, say, 50 KV and a few hundred microamperes.

Jaklevic et al(3) have explored the possibility of using low-powered X-ray tubes with some success. The major contributor of background for these devices is the bremsstrahlung radiation. They were able to reduce this background by using low Z filters or multiple fluorescence geometries.(4)

Goulding et al(5) have developed a number of instrumental improvements which have led to better sensitivities and shorter analysis time. They have developed a guard ring detector to reduce the number of degraded detector pulses due side or "fringing" effects at the solid state Si(Li) detectors edge. By using a double guard ring detector with pulse-reject circuitry the Goulding group has achieved even better results. This latter technique involves requiring a coincident signal between the central region of the detector and the guard ring. This system effectively eliminates the partial collection from the peripheral region of the sensitive volume of the detector. Landis et al(6) have developed a pulsed light feedback system to improve the energy resolution and counting rate performance of the guard ring detector system.

The most effective method for efficiency calibrating X-ray fluorescence systems to do quantitative work is that of using vacuum deposited standards as used in the present work.(4) Giaque and Jaklevic(7) have taken this method one step further by using; the efficiency curve for the detector (obtainable using calibrated radioactive sources) and the values from the literature for the total mass absorption coefficients, photoelectric mass absorption coefficient, the ratio between the photoelectric mass absorption coefficients at the top and the bottom of the K absorption edge, and the fluorescent yield for the element being investigated to develop a semi-theoretical system efficiency curve. They still have to use at least one vacuum deposited standard to normalize their curves.

Goulding and Jaklevic(8) are developing an overall system to use the capabilities of X-ray fluorescence analysis for monitoring the elemental composition of airborne particles. They anticipate using several sampling stations feeding one analysis station. They are planning to use a tantalum-anode X-ray tube to produce bremsstrahlung radiation which will excite one of three fluorescers whose characteristic K-radiation will then excite the sample.

As pointed out in the report from this laboratory last year(4) one of the important features of X-ray fluorescence using radioactive sources to excite with was the potentiality that the system could be made portable. The major reason that present systems are not portable is the requirement that the detectors be cooled with liquid nitrogen. Detectors fabricated from CdTe do not require cooling below normal room temperature and have been developed to a fairly sophisticated level in the past few years.(9-12) The interest in the use of cadmium telluride as a highly efficient room temperature gamma and X-ray detector is due to the high Z, large band gap and relatively good carrier mobility of this material. The high resistivity (greater than 10^6 ohm-cm) necessary to achieve large absorption depths is generally obtained by compensation of the cadmium vacancies and impurities by In or Halogens (Br, Cl, I) during the crystal growing.(13) Because of the large band gap of CdTe (1.44 eV at 300°K) it can be used as a detector in the temperature range -150 to 150° C.

B. Present Work

A higher intensity Pm^{147} bremsstrahlung source was obtained to improve the sensitivity of the X-ray fluorescence apparatus. The new source was comprised of 10 curies of Pm^{147} which yielded 25 millicuries of bremsstrahlung. The source was annular in geometry and is shown in Fig. 1. Because of the different geometry the apparatus had to be efficiency recalibrated. The new efficiency curve is shown in Fig. 2. In comparison with the efficiency curve in our earlier study(4) the new curve is a factor of 100 higher. Since the background is also higher the increased sensitivity was approximately 10.

The experimental work accomplished this year in the Environmental Physics Laboratory at the University of Dayton is discussed in detail in the succeding chapters. Chapter II describes the computer program written and used in the laboratory for routine data analysis. The teletype used with our multichannel analyser is also a terminal for the RCA Spectra 70 computer on campus. This chapter also discusses the need for good ratios of K_α/K_β radiations and some experimental work to measure these ratios.

Chapter III is the description of calculation to determine the effect of sample thickness on the incoming bremsstrahlung radiation. Since the bremsstrahlung is not a quantized radiation this is not a simple calculation. Chapter IV is a detailed discussion of effects on quantitative determinations of sample thickness. In particular the absorption and enhancement effects are examined.

Chapter V presents some recent findings concerning the health effects of trace metals. Chapter VI presents the results of a sediment study of the great Miami River in Dayton, Ohio.

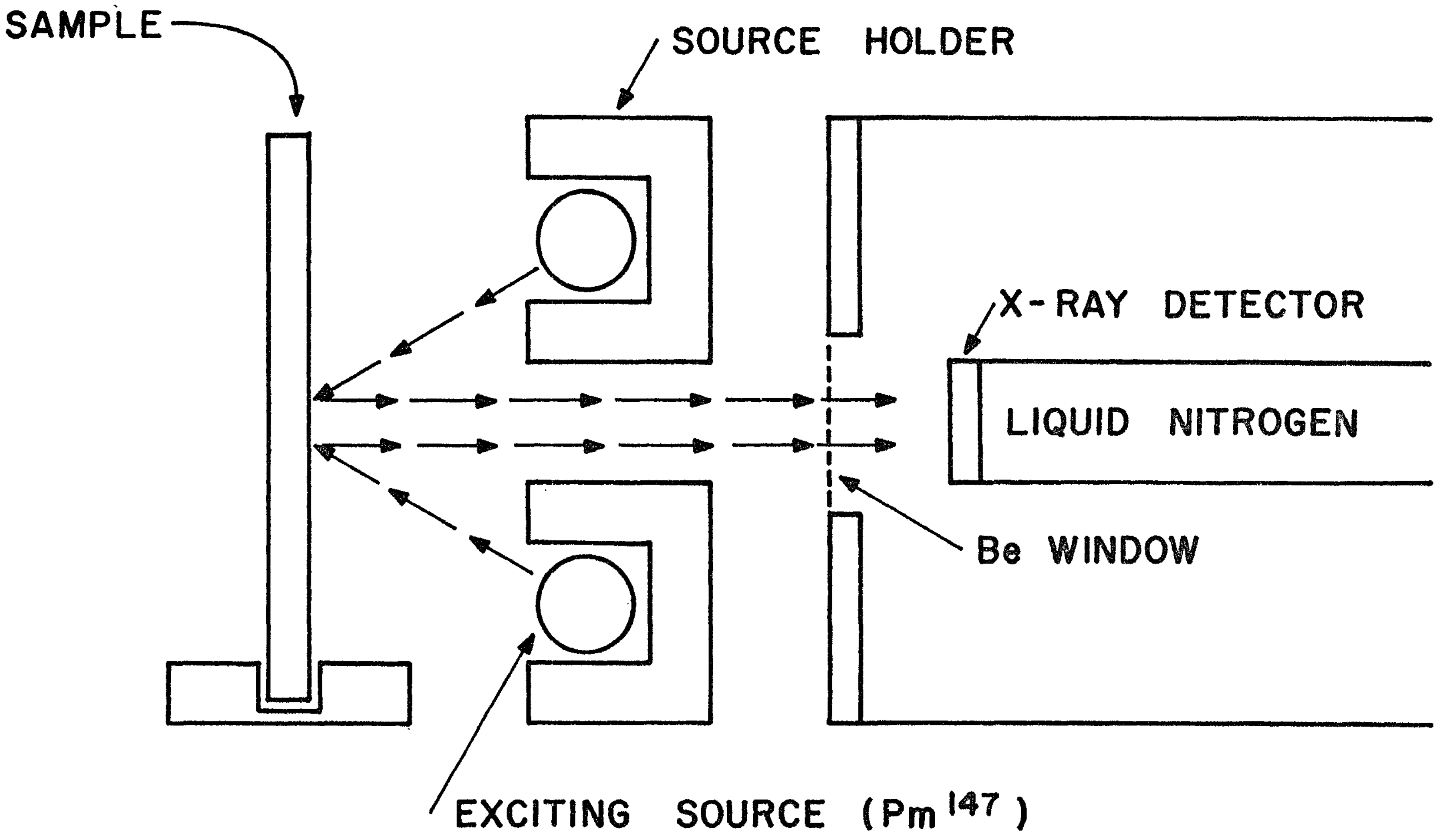


Figure 1. X-Ray Fluorescence apparatus arrangement using the new annular source.

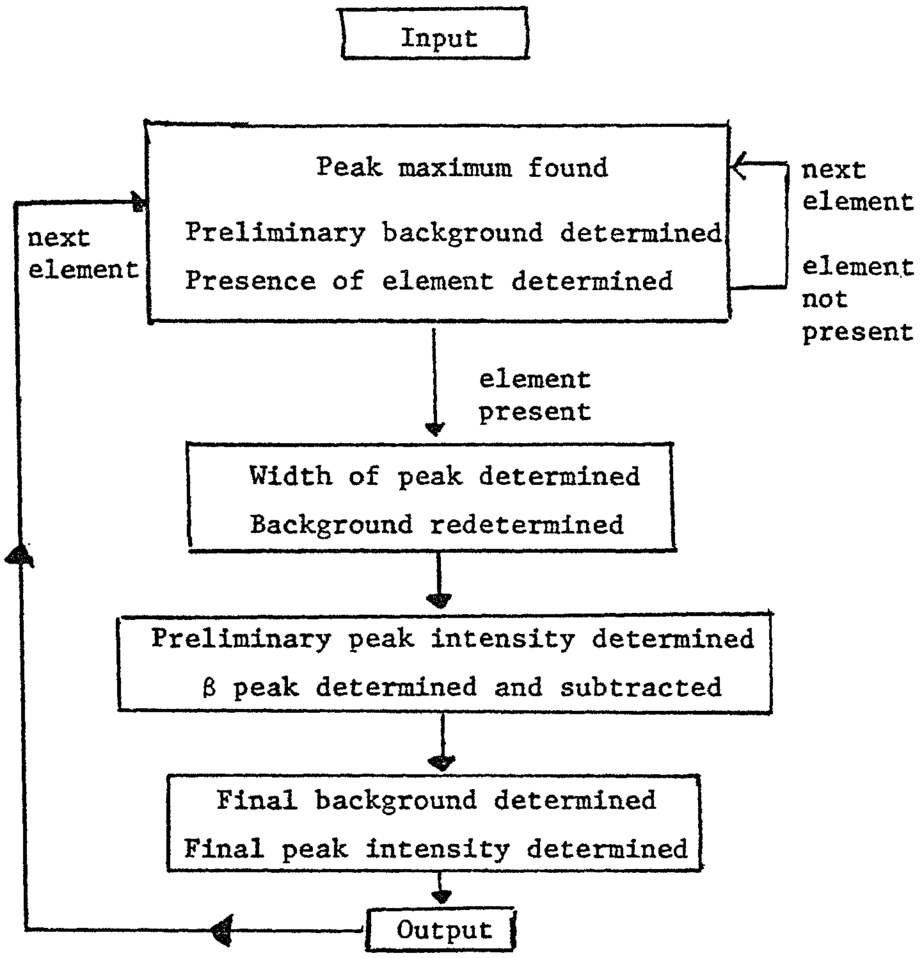
II. COMPUTER PROGRAM FOR DATA ANALYSIS

The data output for each sample involved the output from a 1024 channel multichannel analyser. The analysis of these spectra by hand required roughly one hour per sample. Since the output information was digitized analysis by computer was a logical course to follow. A direct acoustically coupled computer link was attached to the output of the multichannel analyser.

The following is the simplified flow chart of the computer program used (see Appendix for a more complete flow chart). Also discussed as a preliminary of K_α/K_β ratios necessary for the analysis.

A. Flow Chart

Input includes: MCA spectrum, time of run, elements to be analysed for and their expected locations, β/α ratios, number of channels between α and β peaks, and calibration constants.



Output includes: Name of element, channel of the peak maximum, background, peak intensity in total counts and in counts/sec, width of peak, percent error, number of micrograms of the element present.

B. K_α/K_β Intensity Ratios

The computer program's need for the ratio in intensities of the K_α and K_β peaks led to work in this area. Theoretical and experimental work has been done in this area, so our results can be compared to these.

The α/β ratio should be determined by the probability of the transitions which create the x-rays and should be independent of the method of excitation. The K_α x-ray is actually a combination of two x-rays, K_{α_1} and K_{α_2}. The K_β is actually a combination of five x-rays, β_1, β_2, β_3, β_4, β_5. High resolution is needed to separate the β lines, and usually only $\beta_1' = \beta_1 + \beta_3 + \beta_5$ and $\beta_2' = \beta_2 + \beta_4$ are seen. The trasitions which produce the x-rays are

$\alpha_1 = L_{III} \longrightarrow K$

$\alpha_2 = L_{II} \longrightarrow K$

$\beta_1 \quad M_{III} \longrightarrow K$

$\beta_2 \quad N_{III} \longrightarrow K$

$\beta_3 \quad M_{II} \longrightarrow K$

$\beta_4 \quad N_{II} \longrightarrow K$

$\beta_5 \quad M_{IV} \longrightarrow K$

With our system, the β_1' and β_2' x-rays can be resolved only for elements of atomic number around silver (47) and higher. Resolution of the α_1 and α_2 x-rays occurs only for even higher Z, in the area of barium (56).

The probability of these transitions can be estimated theoretically(14) from quantum-mechanical considerations by making assumptions about the processes which cause the transitions. Some experimental values have been tabulated.(15).

For the x-ray fluorescence system used in our laboratory, the α/β ratio is determined not only by the transition probably, but also by the efficiency of the detector. The Si(Li) detector has a definite efficiency vs. energy curve. For low Z elements the correction for efficiency is not too large, since the K_α and K_β x-rays are close in energy. But for higher Z elements, where the energy separation is greater, the correction for detector efficiency becomes important.

A preliminary study of α/β ratios showed a few unexpected and interesting results. Our results were about 10% larger than those of Wapstra(15) for those elements of atomic number higher than strontium. Below strontium our results were smaller than those of Wapstra.

On thick samples a "bump" on the left side of the α peak was observed. At first it was thought to be a scattering effect caused by the thickness of the sample, since it was not observed for thin metal films. However, it is now believed to be caused by the electronics of the system. The thicker samples have a high count rate, and the electronics cannot process the counts quickly enough to correctly record all of them. This was verified by placing a thick metal foil about six inches from the detector (the normal distance is about one inch). The count rate was greatly reduced and a symmetrical peak was obtained. Even so, the effect of sample thickness on the α/β ratio could be interesting.

To determine the effect of sample thickness, copper foils of varying thicknesses were run and their α/β ratios determined. Preliminary results seem to indicate that a plot of K_α/K_β ratios vs thickness of sample is a straight line when plotted on log-log paper. When more points are obtained an analytical function for α/β ratio vs thickness can be determined.

Another unexpected result was obtained with a sample of $SrC\ell$. Although the sample was run and analysed the same way as the pure metal foils, a much lower value of α/β ratio was obtained than was expected. The ratios of the other elements run fit into a smooth curve, but the value obtained for strontium from this sample was well below the curve. It is possible that the form of the sample affected the α/β ratio. The sample was quite thick, and perhaps the thickness caused the different value. Also, the chemical form of strontium may have affected the α/β ratio. There have been some reports in the literature that chemical form may have some effect on x-ray lines. (Roseberry and Bearden, "Effects of Chemical Composition on x-ray Lines," Physical Review, <u>50</u>, Aug. 1, 1936, p.204). To try to detect a chemical effect, finely powdered samples of $ZnSO_4 \cdot 7\,H_2O$ and $FeSO_4 \cdot 7\,H_2O$ were spread as uniformly as possible on scotch tape. Samples of powdered iron and zinc metal were prepared in the same way and the α/β ratios were determined. The samples were checked for homogenity by rotating 180° and redetermining the ratios. No discrepency was found with the rotated sample. The ratios obtained with the compounds and with the pure metals agreed within counting error in all cases.

III. CALCULATION OF THE EFFECT OF ABSORPTION OF NON QUANTIZED RADIATION

One of the contributions to the quantitative uncertainty is the effect of absorption of the incoming excitation radiation and the emerging x-rays. In order to calculate the magnitude of this effect for the present apparatus one needs knowledge of the following details; detector and system efficiency and the variation of the obsorption coefficient as a function of energy. The major complication in calculating the effect of absorption is that the excitation is not quantized in energy. That is the energy distribution of

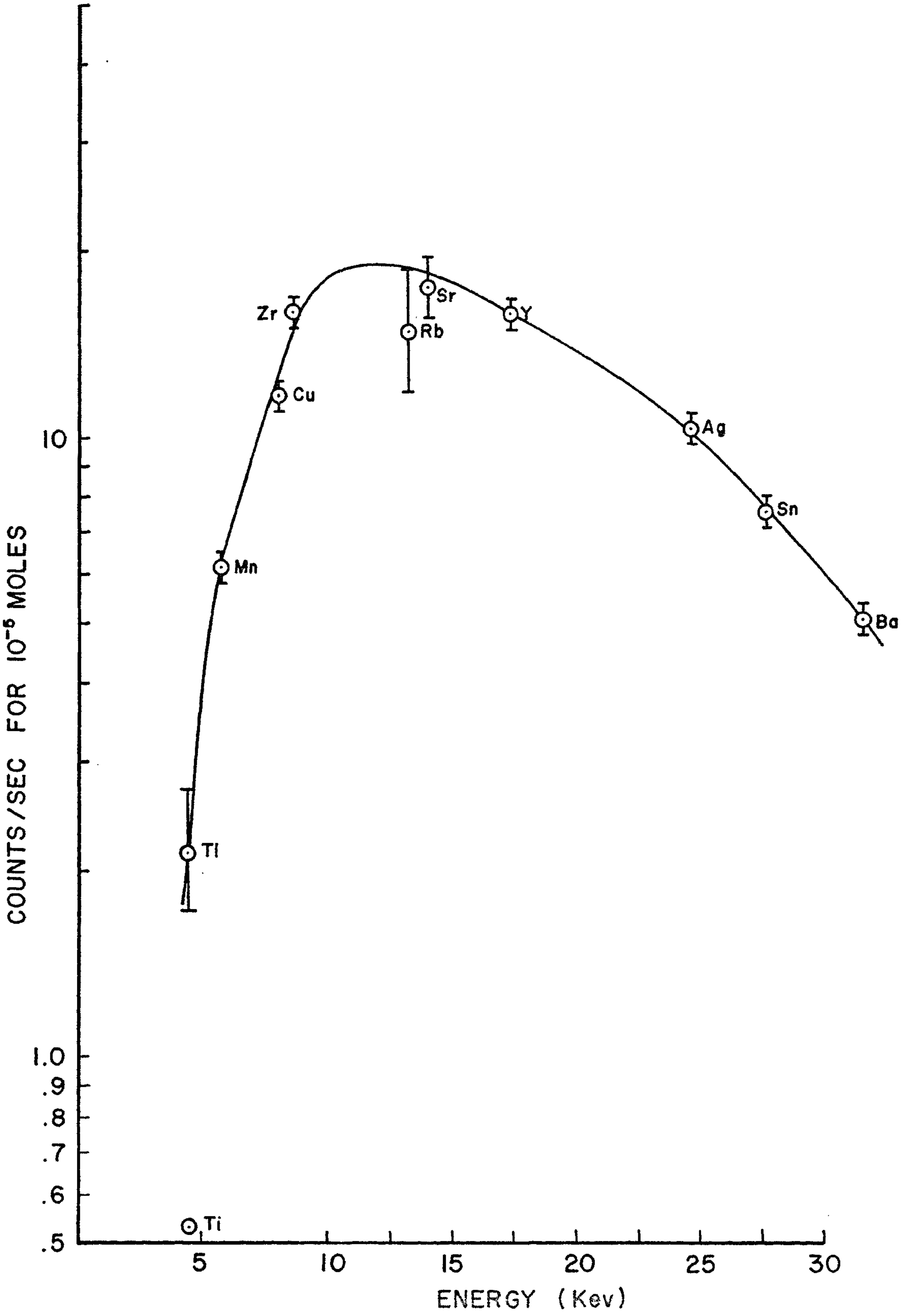


Figure 2. Efficiency curve resulting from the new Pm^{147} source.

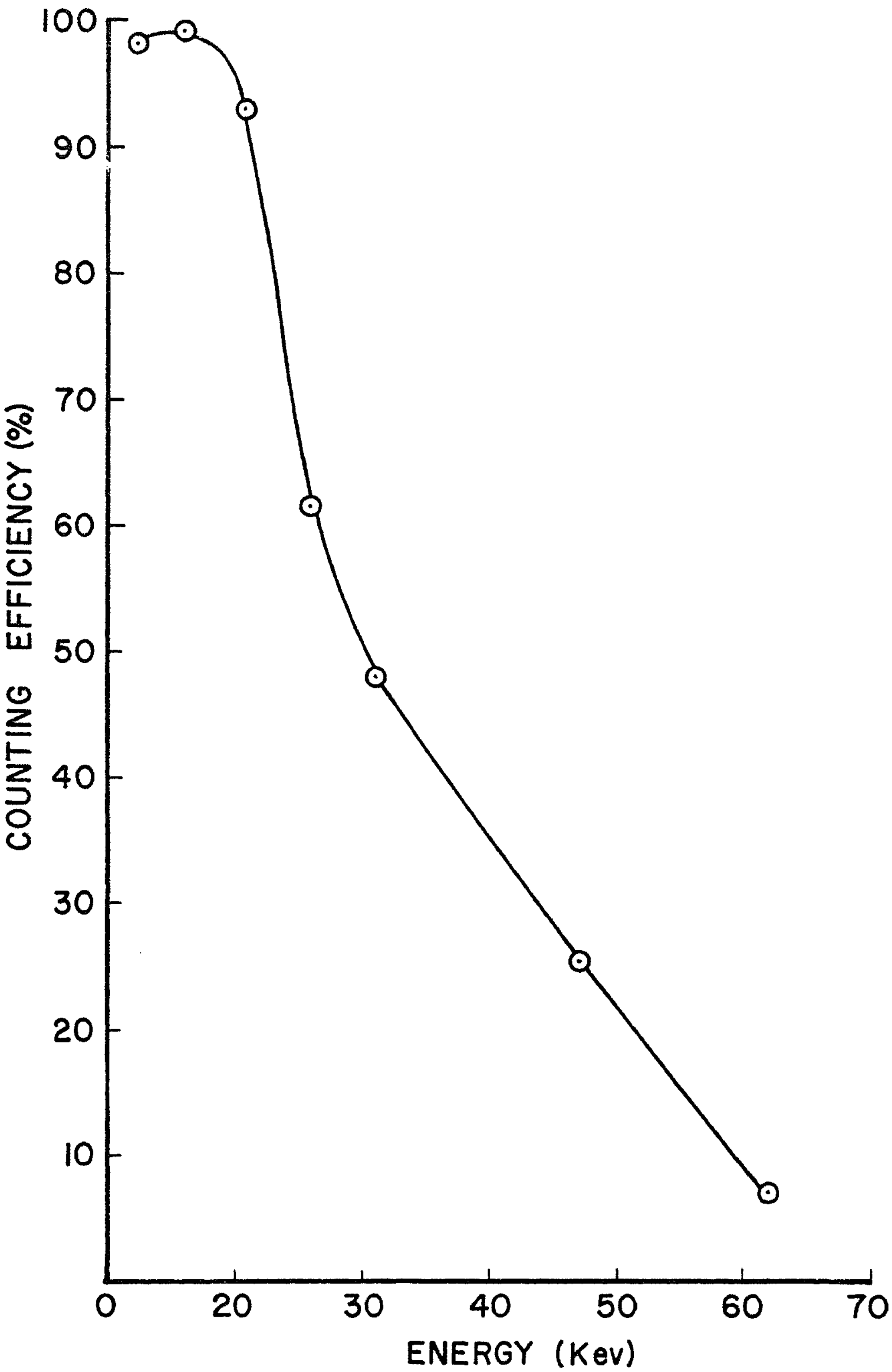


Figure 3. Efficiency of the Si(Li) detector taken from Fig. 1-4 of the Ortec (100 Midland Rd., Oak Ridge, Tenn.) Spectrometer system instruction manual.

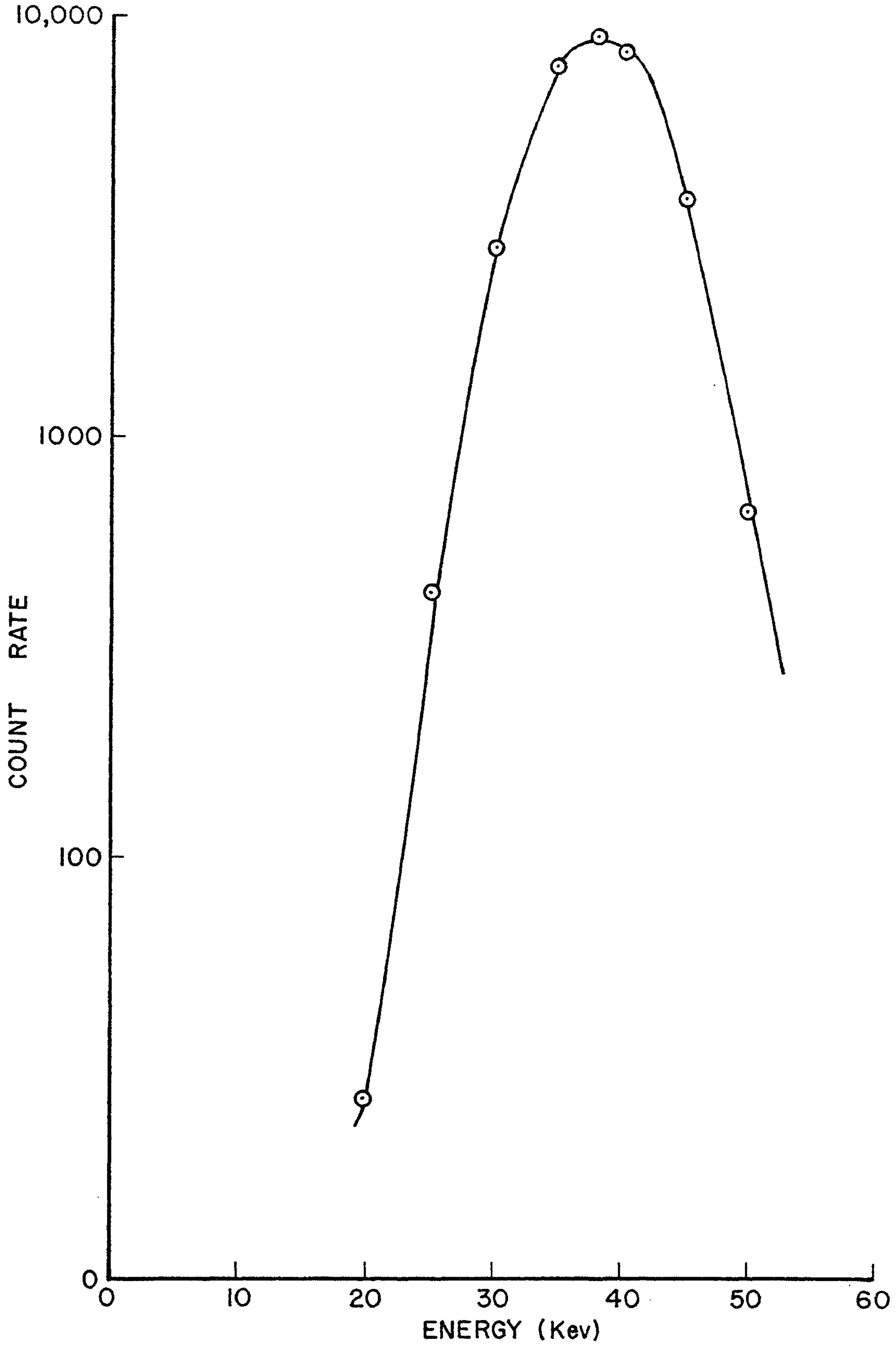


Figure 4. Energy spectrum of the exciting source corrected for detector efficiency.

the exciting source must be folded into the absorption coefficient curve.

The counting efficiency of our system varies with energy and is described the curve in figure 3. Figure 4 shows the energy versus counts for our source aimed into the detector, with the efficiency of the system removed. To do this the actual number of counts for a given energy was divided by the efficiency of the system at that energy. Therefore, figure 2 shows relative amounts of each energy given off by our exciting source. The equation of this curve was found to be best approximated by

$$y = 9000e^{-.018(x-38)^2} \tag{1}$$

The equation of the curve of absorption coefficients for iron (cm^2/gm) versus X-ray energy was approximated by

$$Kv = 5.52 \times 10^5 \times (x^{-3}) \tag{2}$$

The absorption coefficient must be calculated for the whole range of incoming energies. The relative amounts of these energies given off are given by (1) so by integrating the product of (1) and (2) and dividing out the integrated weighting factor (1), the coefficient can be found.

Therefore, the absorption coefficient for iron in a range of 20 to 50 keV (which is the range of energy given by our source) is given by

$$\frac{\int_{20}^{50} 9000e^{-.018(x-38)^2} \; 5.52 \times 10^5 \times (x^{-3})\, dx}{\int_{20}^{50} 9000e^{-.018(x-38)^2}\, dx}$$

This integration was approximated using the Trapezoidal Rule where

$$\int_a^b f(x)dx \approx \left(\frac{y_0}{2} + y_1 + y_2 + \dots + y_{n-1} + \frac{y_n}{2}\right)h$$

where $y_i = f(a + ih)$, $i = 0, 1, 2, \dots n$.

A simple basic computer program was written to calculate y_i's. Error is given by

$$\left|\int_a^b f(x)dx - T\right| \leq \frac{b-a}{12} \quad mh^2$$

where T is the approximation found above and $|f''(x)| \leq m$. Error here is 18%, for an absorption coefficient of 10.6 (cm^2/gm).

Assuming a typical water sample area of 75 cm^2 for a weight of .1 gm, the fraction of x-rays absorbed is given by

$$1 - e^{-(10.6)\frac{cm^2}{gm}\left(\frac{.1\ gm}{75\ cm^2}\right)} = 1 - e^{-.014} = 1 - .986$$

$$= .014 = 1.4\%$$

This value is for iron (Z = 26) assuming the excited atom is approximately at half thickness of the sample. The absorption coefficient for another Z can be found by replacing eq. (2) with the proper equation given by the plots in Graphs of X-Ray absorption Coefficients.$^{(16)}$

As can be seen from the above calculation the effect of absorption of a lower Z element on the excitation radiation involving parameters typical of the water samples examined in this study is roughly an order of magnitude smaller than the overall experimental errors. Thus in general it is justifiable to ignore the effect of absorption on the incoming excitation radiation.

The effect of absorption on the out going X-rays if in the above case one considers the iron line is larger than that on the excitation radiation. For example assuming the sample vs Z = 20 and an iron atom at half thickness is excited, the absorption of the outgoing X-ray is roughly 33%.

IV. STUDIES OF ABSORPTION AND MATRIX EFFECTS

A. INTRODUCTION

This section describes the research conducted to study what are known as absorption effects and matrix effects. The work was done from a point of view relative to all the work done in the lab. The underlying reason for studying these effects was to determine their relation to the quantitative accuracy of the results of other projects, and in particular, the effect upon results of concentrations of trace metals in river water.

Absorption effects become significant when the thickness of the sample is large enough that the elements in the front of the sample absorb all of the incoming radiation which prevents elements in the back part of the sample from becoming fluoresced. Ordinarily the sample would be thin enough that all of the atoms of the elements would be fluoresced and an accurate analysis could then be made. When all the elements are not fluoresced they are not detected and therefore the quantitative results fall short of yielding accurate concentrations of elements in the sample. The question to be answered in this project centered around determining the range of sample thicknesses being used in all the areas of trace metal research taking place in the lab. That is, are the sample thicknesses that are being used in the lab in the range where absorption effects become significant?

Matrix (e.g. enhancement) effects deal with another phenomenon which can take place despite the thickness of the sample. The effect is basically one in which an initially fluoresced element gives off its characteristic energy which, instead of being directly detected, fluoresces an atom of an element of lower Z (atomic number) and this element becomes detected by the system as it gives off its characteristic energy. As a result, the higher Z element in the final analysis is shown to have a lower concentration and the lower Z elements become enhanced. The work in this area was geared towards determining the size of this effect.

As a result of work done in the two above-mentioned areas other side projects arose in removing stumbling blocks and problems which arose in the project. These side projects included a study of the weight loss of a sample during the filtering process, a study of the weight loss in a sample over a period of time, and a study of the fluctuation of filter paper weight as a function of time and possibly temperature. All of these areas and the experimental techniques used in investigation are discussed. It is assumed that the reader, for the most part, is familiar with the general process of the x-ray fluorescence technique and its apparatus along with the basic sample filtering apparatus.

B. INTROUDCTORY WORK

In the early stages of the project effort was made to gain a background in the areas to be investigated. Articles and sections of books were read which were related to the areas investigated. Below is a series of short summaries of the readings. In many cases simple pertinent quotations were lifted from the text of the articles and served as the summary of the article. The ordering of these reports is not an alphabetical one, but a chronological one, that is the order in which the articles were read.

1. Gilmore, Forest R., "Graphs of X-ray Absorption Coefficients for Fourteen Substances",(16)

The report is a collection of experimental and theoretical values for the x-ray absorption coefficients of Be, C, N, O, Al, Fe, Cu, Ag, tin, gold, lead, uranium, air and sodium iodide in the energy range from 0.1 to 100 kv.

2. Rhodin, T. N., "Chemical Analysis of Thin Films by X-ray Emission Spectrography."(17)

Article discusses the process of depositing metal by vaporization of high purity material in a vacuum. The oxide films were formed by floating metal films reinforced with Formvar into a solution of 5.0% nitric acid and .5% Potassium Dichromate at 60° C for periods from between 30-100 minutes. The reinforced films were then scooped into Mylar and metal. Surface film densities were calculated from weight and accurate measures of area. "The conclusion is made that accuracies within 2% or better can be obtained for the chemical analysis of such highly dispersed samples by x-rays without the application of corrections for absorption deviations."

3. Wilson, H. N., "An Approach to Chemical Analysis" (18)

p. 308 Good example of the Matrix effects problem.

p. 305 General thickness considerations.

p. 307 Discusses quantitative analysis by adding known amounts of the elements to be investigated."....it is perhaps particularly in ferrous metals that inter-element effects are most pronounced.

4. Giauque, R. D., "A Radioisotope Source - Target Assembly for X-ray Spectrometry."(19)

p. 1 Major problems in analysis-matrix enhancement and absorption effects see p. 3 also.

5. Sherman, J., "The Theoretical Derivation of Fluorescent X-ray Intensities from Mixtures."(20)

   p. 283 Mutual enhancement effect discussion.

   p. 284 example uses Cr, Fe, Ni.

   p. 286 an "infinitely" thick specimen is used.

   Absorption coefficent has units of cm^2/gm.

   p. 286 fluorescent intensity integrals are given for three component mixtures.

   A mathematical model for final intensities of mixtures is given.

   p.294 Computed and observed intensities ratios are given. Note: Stiff math is used in the calculations but the comments may be useful for matrix effects work although the work done for this report is in large percentages, not ppm.

6. Cothern, C. R., "Determination of Trace Metal Pollutants in Water Resources."(4)

   The entire manual serves as an introduction to the work being done in the lab. Absorption effects are specifically mentioned with respect to absorption coefficients on p.27f and matrix effects are discussed briefly on p. 39.

7. Alley, B., Myers, R., "Calibration Method for the X-Ray Fluorescence Analysis of Multicomponent Mixtures."(21)

   Simple lattice designs for experimental situations involving mixtures are discussed. Analysis of mixtures is given which contains math and also matrix models. The discussion includes a root mean square error analysis. Some graphs of the simple calibration curves are given.

8. Adler, "X-ray Emission Spectroscopy in Geology."(22)

p. 206-207 A brief mention of mass-absorption coefficients and how they enter into the absorption correction is given for quantitative micro qualitative analysis. A brief mention of background intensities and enhancement is also included.

9. Mitchell, B., "X-ray Determination of Zirconium, Tungsten, Vanadium, Iron, Titanium, Tantalum, and Niobium Oxides."(23)

p. 1653 The number of standards was kept to a minimum by use of a correction factor method of interelement correction. The article may be useful because it has calibration curves for seven of the elements which are in the range of elements with which we may eventually work.

10. Adler, "X-ray Emission Spectroscopy in Geology," ch. 7(22)

p. 110 "As the film (sample) gets thicker it begins to reduce the intensity of both the incident primary beam and the emerging secondary energy beam." Therefore, the intensity of the analytical line is altered by the thickness of the sample. Because these analytical lines and their intensities determine the quantitative results of the sample being analyzed, the sample thickness directly affects these quantitative results and a need to know the affects of the sample thickness becomes apparent.

11. Morrison, George H., "Trace Analysis: Physical Methods."(24)

p. 131-133 In particular there is a discussion of methods of precipitating Cu, Fe, Pb, Mn, Ni, Sn, Zn as low as .1 ppm. The author gives reference for this technique: Dehm, Dunn and Loder, Anal. Chem., 33, 607 (1961)

12. Luke, C.L., "Determination of Trace Elements in Inorganic and Organic Materials by X-ray Fluorescence Spectroscopy."(25)

This article describes a method for gaining ppm concentration of certain trace metals by use of a coprecipitation technique in which one element is precipitated out in a small concentration along with a relatively large concentration of the co-precipitator.

"...By use of preliminary separations, it is possible to isolate the trace elements from the matrix elements or from elements which will cause line interference; second, by use of a coprecipitation element and a suitable precipitating reagent it is possible to precipitate the trace metals quantitatively; and, third, by arranging to isolate the trace elements, uniformly dispersed in a low atomic number matrix, interelement absorption and enhancement is virtually nil."

C. ABSORPTION EFFECTS

The purpose of investigation in this area is to verify a constant linear relationship between the thickness of the samples used and the intensities of the spectra obtained from these samples. The calibration of the system resulting in accurate concentrations for the actual amounts of trace metals in the sample is dependent upon this linear relationship.

Experimentally it has previously been found that as the thickness or amount of material in the sample is increased the concentrations detected increase proportionally.(4) That is, if the amount of material in the sample was doubled, the concentration detected would have also doubled. However, it was suspected that a point would be reached where the linear relationship would cease due to a too highly concentrated sample. This phenomenon occurs when the sample becomes so thick or dense that the incident or exciting x-rays are completely absorbed before reaching all of the atoms within the sample. In this case not all of the atoms are fluoresced. An illustration of the linear relationship, the saturation point and what relationship exists beyond this point is found in Figure 5. The questions which arise and prompt the present research are first, where does this point of saturation occur and second, into which region of sample weight does the work in the general project fall?

To begin answering these questions we refer to work done previously in other areas of the overall program.(4) In these calibrations relatively small concentrations were used of just one element and the results obviously fell safely into the linear range. Research was continued specifically in regions of higher concentrations where actual river water samples were used along with lab prepared samples of a CuS precipitate.

Whereas previous work done with copper had used samples of weight maximums of 1.8 mg, the work done with the CuS precipitate started with samples of weight 1.0 mg and continued through samples with a weight near 6.0 mg. The CuS precipitate was gained through a chemical qualitative analysis technique.(26)

The reasons for selecting CuS as a precipitate containing only one trace metal are numerous. Needed was a precipitate which could be easily obtained, easily precipitated and totally precipitated. Also of importance was the idea of being able to end up with a precipitate whose element concentrations were known. CuS fills, for the most part, all of these requirements. Its failing will be discussed in a later section. The most

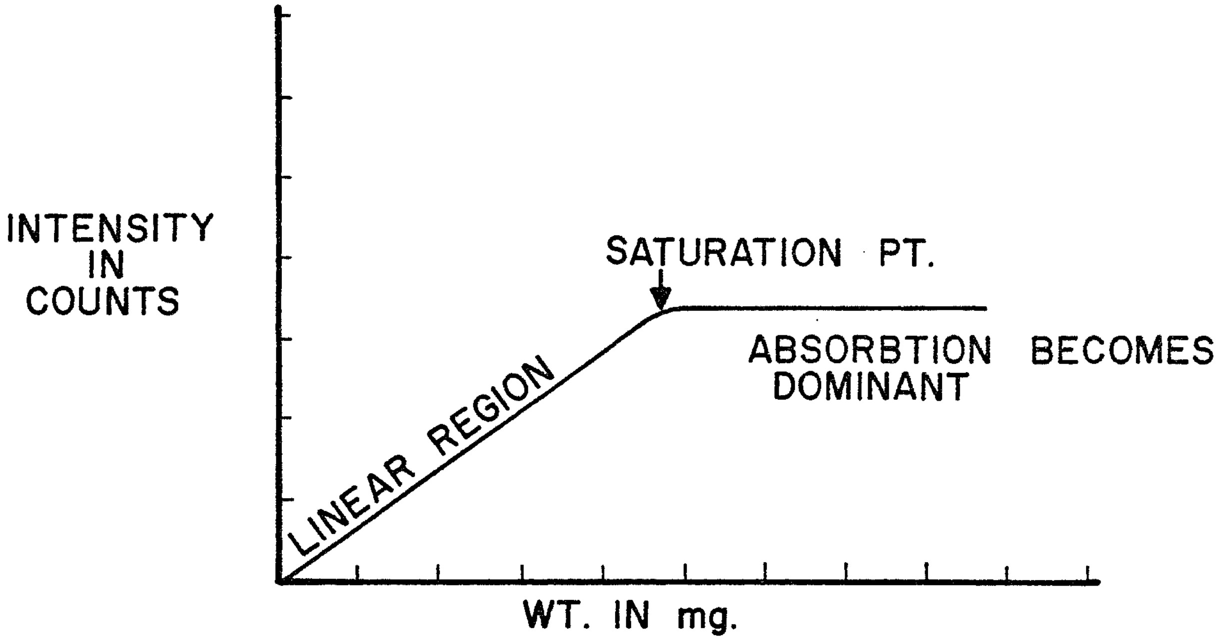


Figure 5. Illustration of the linear relationship between the amount of sample intensity, the saturation point and the following region.

significant reason for the use of this technique was the total precipitation of the copper. This total precipitation was guaranteed by calculations using the solubility product.(27) Knowing this, samples were prepared and analyzed yielding results which are summerized in Table 1 and in Figure 6. It can be seen from this data that the linearity holds for the area of concentrations investigated.

The purpose of running river water samples was to continue the concentration range into the area of 20-30 mg. Two separate batches of the of the river water were obtained and two separate groups of samples were obtained and analyzed. The results from one of these samples are found in Table 2 and in Figure 7. The set of data found in Table 2 yields interesting results as can be seen in Figure 7. The plot of intensity vs ml of river water sample yields a curve which resembles a parabola, that is, a quadratic relationship. This type of relationship rules out the possibility of absorption effects being significant in this range. This particular effect has been found before and has a somewhat simple hypothetical explanation.(4) In the range of larger amounts of river water poured through the filter paper it is possible that particles small enough to get through the 8 micron hole filter paper were trapped by the build up the sample on the filter paper. That is, perhaps the larger particles trapped by the filter paper served as another means of filtering out the smaller particle which previously had escaped the filtering process. According to this hypothesis, then, the intensities of the larger condentrations would no longer hold to the simple linear relationship.

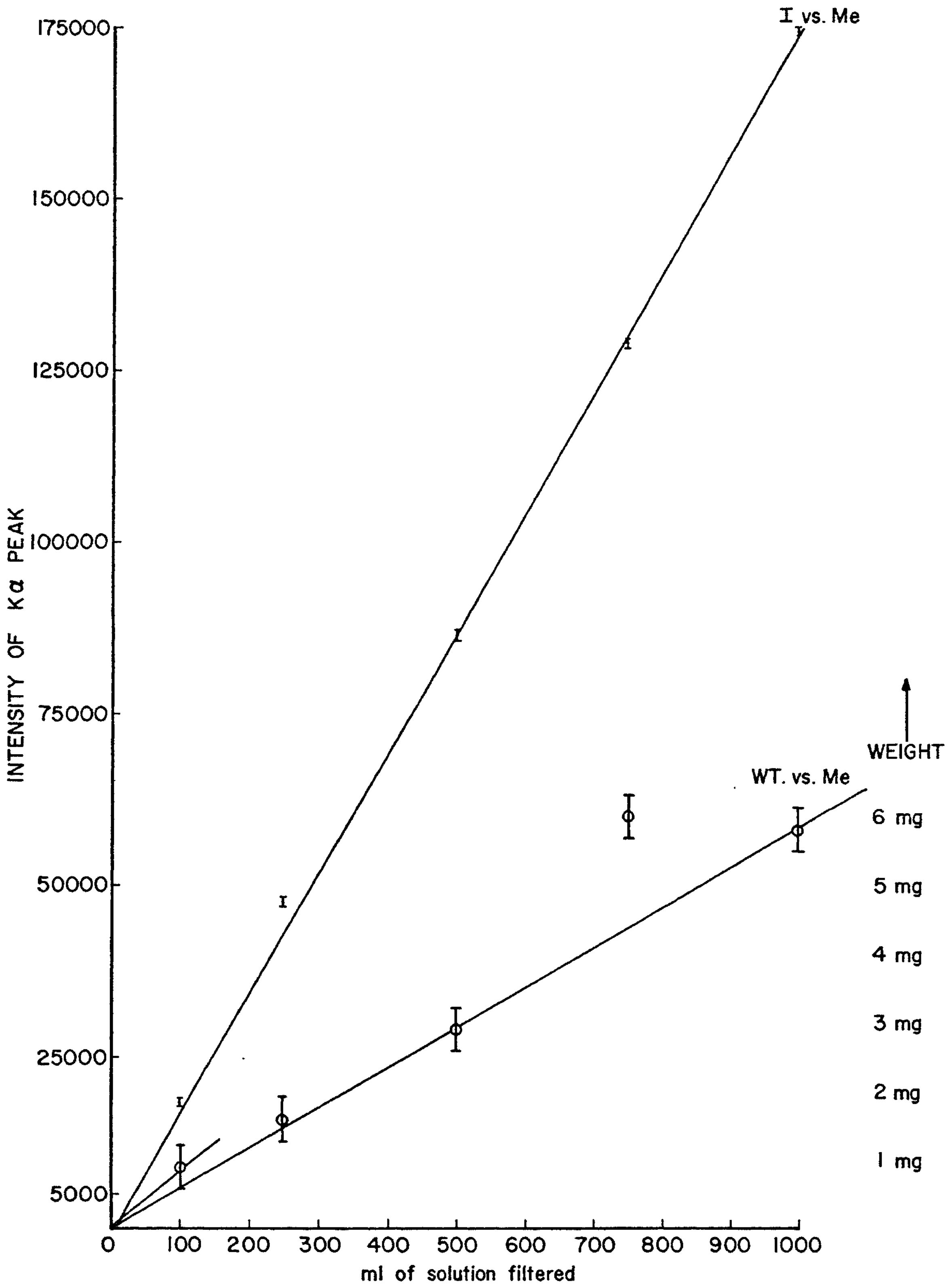


Figure 6. Intensity and weight as a function of volume of CuS solution filtered.

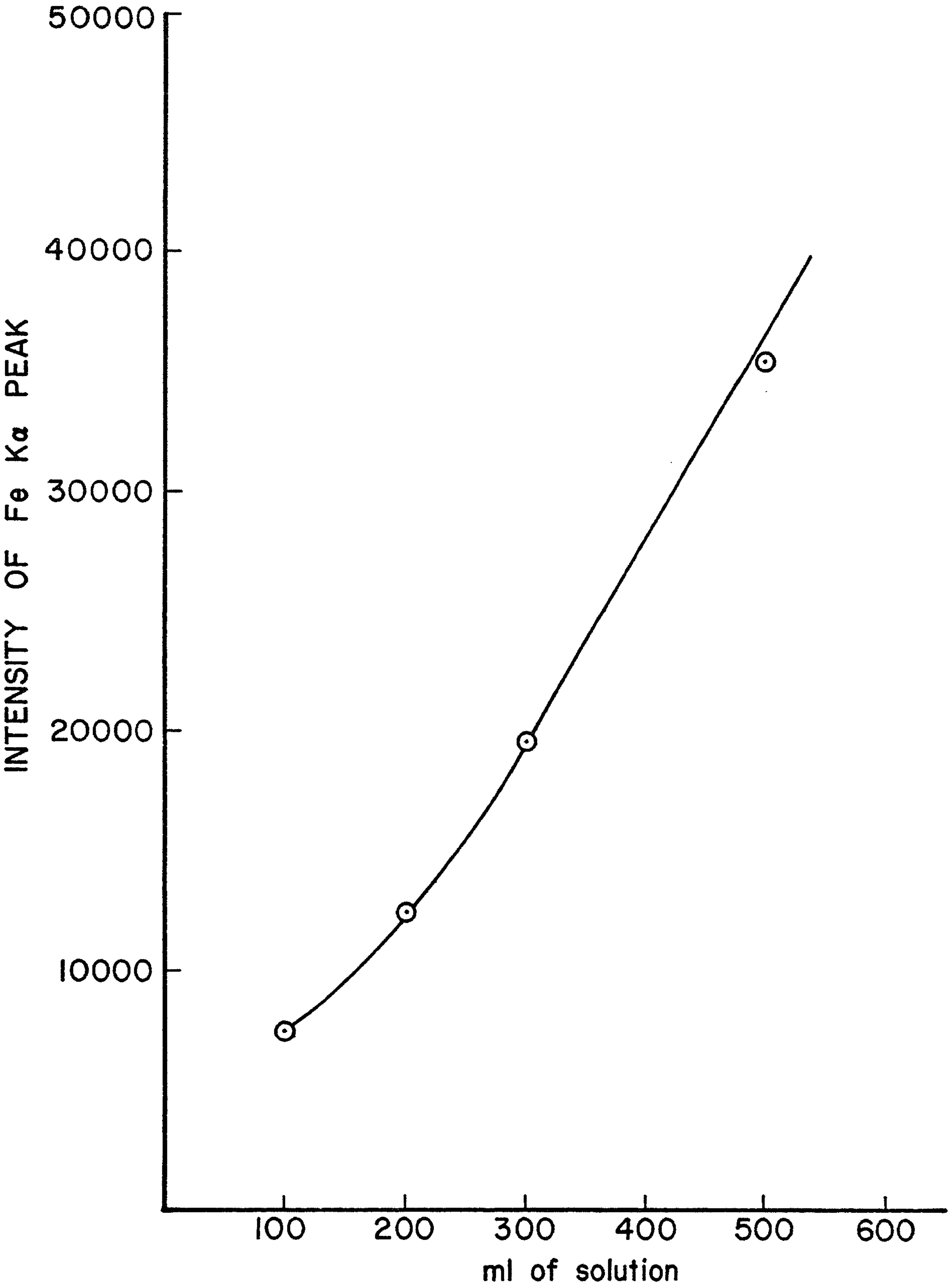


Figure 7. Intensity of Fe K_α peak as a function of the volume of solution filtered. From river water sample #17 collected Oct. 20, 1971. The errors are within the circles shown. The points are best approximated by a quadratic function.

Although it is concluded from these experiments that the range of concentrations used in the lab projects fall safely in the linear range, it should be mentioned that a saturation point was not reached in any of the experiments. To find a saturation point is the purpose of future work. It should be noted here that the samples used taxed the filtering system and that any efforts to obtain thicker samples should be made using a compressor of some kind instead of a vacuum pump.

D. MASS-VOLUME RELATIONSHIP

It should be noted here that the goal of all the studies in the absorption effects area was to obtain results which were accurate with respect to the actual concentration of trace metals in the environment. In lab work analysis systematic errors may arise. One such possible systematic error was investigated. Inherent in the study of absorption effects is the correlation of ml of actual sample poured through the filtering apparatus and the weight of sample, in precipitate form, on the filter paper. Once again a direct proportionality is needed in order for the results obtained through analysis to be relevant to reality.

For preparation of samples for analysis, the liquid sample, measured in ml, is poured through a filter paper depositing material measured in mg, on the paper. The relationship between ml and mg was investigated and the results may be found in Table 1, with an illustration in Figure 6.

It was found that not only was the relationship between mg and ml proportional and linear but that the proportional and linear but- that the proportion between intensity and ml equaled that of mg and ml within experimental error.

These results show a direct relationship among the weight, ml of sample and peak intensity. This result not only validates our work in this area, but makes discussion and calculations more convenient.

E. SIDE PROJECTS: WEIGHT LOSSES

In conducting several of the experiments mentioned previously several questions arose concerning weight loss in the filtering technique and weight fluctuations of the filter paper and of filtered samples. Results of the investigation of these areas proved significant.

The first area of investigation concerned itself with the possibility of precipitate loss in the filtering process.(8) The question arose as to the loss of precipitate when the previously mentioned CuS samples were being prepared. A certain amount of precipitate was expected to be deposited on the filter paper at the end of the process. However, as the data in Table 3 show, a large portion of the precipitate was being lost somewhere in the filtering process. To pinpoint the losses to the actual filtering process, a sample was prepared strictly of iron filings and the percentage of weight loss tended to be in the same area. Although this loss does not effect the use of the filtering process for preparing samples for the study of absorption effects, the loss discourages and eliminates its use for the study of matrix effects. The loss is apparently due to the precipitate settling around the sides of the filtering device. Although the area was not investigated to the point of verifying the quantitative accuracies of the values found for weight loss, it is of a sufficient amount to merit future study in this area.

Another question which arose dealt with the area of filter paper weight fluctuation over a period of time. In experiments involving small amounts of sample these possible fluctuation may be significant. The data taken in the brief study of this question may be found in Table 4 and it shows that the possibility of the fluctuation of filter paper weight with time, temperature and probably even humidity. Once again the study only points out the need for more work in this area.

A final question in this area deals with the fluctuation of the weight of a prepared sample with time. Prepared samples were weighed over a period of approximately a month and the results showed that the fluctuations were very slight. Apparently the weight fluctuation of a sample is small with the fluctuation of the weight of a filter paper alone. This may result from the presence of the precipitate which may retard the fluctuation processes of the filter paper alone, such as moisture absorption, etc. The data from this study is found in Table 5.

F. MATRIX EFFECTS

The goal of the work involved with matrix effects is a more simple one than that of the thickness studies. In this area of study the purpose is to discover how much the concept of matrix effects actually affects the quantitative results of analysis. Although the goal is simple and straight forward, developing a technique for studying these effects is a much more difficult job. In general, the idea of the research is to obtain samples containing known concentrations of trace metals in a matrix of known components. The overall sample should be similar to an authentic river water sample in order that any conclusions drawn from analysis of the artificial samples may be applied to actual river water samples. The main drive in the research was to determine a method for obtaining samples similar to those described above. To date the research has centered around two methods for obtaining the samples.

The first process, which was short-lived, was a carry over from the study of thickness effects. The process involved the exact same technique as the one used in obtaining the CuS samples. A known amount of copper would be initially obtained and then precipitated and finally filtered onto a filter paper for analysis. The overall plan was to then develop similar techniques for other trace metal elements and then combine trace metals of known amounts in the same sample and check for the expected matrix effects. Before this could be done, however, the areas of weight loss which were discussed in the previous section made the process unsuitable for the study. The basic ideas of the experiment remain sound; another technique for obtaining and mixing known amounts of trace metals was sought.

The feasibility of a second method for obtaining the desired samples was tested and is still being tested. The technique involves placing trace metals which exist in powdered compounds onto clear adhesive tape which already is mounted on an aluminum ring which is used in mounting the entire sample near the source and detector for the purpose of analysis. This technique has been conveniently coined the "Scotch Tape Technique."

The basic process, the reason behind it and the expected results are the following. If two powdered compounds containing different trace metals could be mixed in known quantities where the ratio of the amounts of the two trace metals could be determined, then possible matrix effects could be studied. For instance, if two compounds with known contents of different trace metals could be prepared and analyzed then the ratio of the intensities of the peaks of each element should be equal to the ratio of the known amounts of the trace metals in each compound. If matrix effects occur, however, it is expected that the metal of lower Z would have its intensity enhanced while the other element's intensity would be decreased. This would result in a different ratio of the peak intensities. This theory was investigated experimentally.

Before any experiments of this nature could be carried out, however, a number of possible stumbling blocks had to be investigated. Since the primary purpose is to isolate the matrix effects, all other effects should be minimized. Since the enhancement effects will be detected by changes in the ratios as discussed above, it is necessary to minimize all other factors which may affect this ratio of intensities. Some possible variance factors include the uniformity of the sample on the tape, the homogeneity of the sample mixture, normal statistical fluctuations, and the possibility that the error in the amount of trace metals in the sample can exceed the change in the intensities in the matrix effects.

In the first attempt to estimate the role of sample uniformity in the alteration of the ratios powdered iron and copper were mixed and placed on tape for analysis. To check uniformity 3 different runs were made on the same sample with the sample rotated 90^o for each run. Significant changes in the ratios were found and a lack of uniformity and homogeneity of the sample were blamed. In the experiments which follow a check for uniformity is included and the affect upon the ratios were determined. Careful attention was paid in each of the experiments to determine that the changes in the ratios of the intensities were not largely dependant upon variance factors listed above.

In the actual experiment samples were prepared of different ratios of two compounds; $FeSO_4$-$7H_2O$ and $ZnSO_4$-$7H_2O$. Varying ratios were prepared in order that the possible increase of matrix effects with increasing ratios of trace metals could be studied. Five mixtures were run and one of the mixtures was run a second time rotated through an angle of 180^o as a check for the uniformity of the samples. The results of these runs may be found in Table 6.

As can be seen from the results, the results were not at all what was expected. In the table the ratios of zinc over iron are given and since iron is of lower Z, it is expected that the ratio of the intensities would decrease as a result of the iron's concentration becoming enhanced and the concentration, as seen by the detector, of zinc becoming decreased. Certainly these results offer no information as to the affect of the matrix effects. Instead it is now the job here to investgate the possible causes of such inaccurate results.

The first area suspected to be the culprit was the uniformity of the sample. However, in comparing the ratios of the two runs made for checking the uniformity of the samples it can be seen that the change in the ratio of the sample due to rotation is small when compared to the overall change of the ratios.

A second area of investigation centered around the efficiency of the detector.(4) The efficiency curve indicates how much of the detected characteristic energies are actually being recorded and counted. The efficiency of the detector in the range of zinc is found to be approximately 95%. The efficiency of the detector in range of iron is approximately 90%. Therefore 5% more zinc is being detected which would tend to increase the ratio. However, a 5% difference is not significant when compared to the deviation of the ratios of intensities from the calculated and expected results. Therefore, other areas introducing the change of ratio need to be investigated. One possible area is in the preparation of the sample. It is possible that the sample is not a uniform mixture of the two elements, or in preparing the samples the ratios which end up on the tape may be different than the ratios which are prepared in bulk and from which calculations are made.

Although this method for obtaining sample shows a great deal of promise, it is necessary to do a great deal of work in refining this technique for preparing the samples. Also many samples of varying compounds in varying ratios need be analyzed before any definite conclusions concerning Matrix effects can be drawn.

V. HEALTH EFFECTS

The following discussion involves reference information supplemental to that contained in the 1971 report concerning the toxic and health effects of some of the elements detected in the present study.

Vanadium

The 24 hr LC_{50} (the amount that kills 50% of the fish within 24 hours) of orthovanadate was 14 ppm. For metavanadate it was 50 ppm. Concentrations lower than those tested might have been lethal to fish after prolonged exposure(28).

No toxity was demonstrated by tetravalent vanadium for rats. Vanadium pentoxide in drinking water was highly toxic to rats at 49 ppb. The valence state of this metal may influence its toxicity(29) to 2.5 ppm Cr^{+6}. The acute minimal lethal dose in dogs for chromic acid is stated as 330 mg/kg for intravenous sodium chromate, corresponding to 75 mg of the element. The latter salt causes preterminal hypotension, hypocholesteremia, and hyperglycemia. Chronic toxicity was observed in several species with Cr^{+6} in concentrations of more than 5 ppm in the drinking water. Grushko (28) found subacute toxicity and accumulation of chromium in the tissues of rabbits that were given 5 ppm (as chromate) in the drinking water. The element accumulation also in rats when given at this level, but caused no changes in the growth rates, food intake, or blood analysis. Even 25 ppm in the drinking water failed to produce changes in these parameters or in the histological appearance of the tissues after 6 months. Dogs tolerated up to 11.2 ppm of Cr^{+6} in the water for 4 years without any ill effects. Growing chickens showed no detrimental symptoms when they were fed 100 ppm in the diet.

Toxicity of trivalent chromium appears to be restricted to parenteral administration. No reports of oral toxicity of trivalent chromium are known. All these results point out the very low toxicity of chromium except for poorly soluble chromates directly implanted in tissues in very high amounts or deposited in the respiratory tract. The therapeutic:toxic ratio for intravenously injected Cr^{+6} is approximately 1:10,000.

Chromium is poorly absorbed in the gastrointestinal tract, the hexovalent better than the trivalent form. Affinity for testes, bones, liver, and spleen is high: that for muscle and brain, low. Although poorly soluble chromate dusts lead to increased incidence of respiratory diseases, the toxicity of soluble hexavalent and trivalent compounds is very low.(30)

Nickel

Nickel is of low toxicity to fish. The 12 day LC_{50} is .5 ppm.(31)

Copper

Copper in ionic form is very toxic to the photosynthesis of the green alga, chlorella pyrenoidosa and the diatom, nitzschiz palea, in concentrations of copper normally found in natural waters, indicating that copper is not ordinarilly present in ionic form but is complexed to organic matter such as polypeptides.(32)

Copper concentrations of .04 ppm were acutely toxic to chinook salmon fry and concentrations of .02 ppm increased mortality and inhibited growth. The maximum acceptable concentration for the flathead minnow is between .03 and .08 ppm.(33) The survival of gammarus, an invertebrate, was markedly decreased between 12.9 and 6.2 ppb. Newly hatched amphipods grew to the adult stage only in concentrations less than or equal to 4.6 ppb.(34)

Concentrations between .56 and 3.2 ppm resulted in the fatty metamorphosis of the liver, necrosis in the kidney and gross changes in gill architecture in the winter flounder. A concentration of .18 ppm produced and extracted appearence in the gill lamellae. The epithelial layer appeared vacuolated, the basilamellar region was reduced in thickness and the lamellar mucus cells were few, while chloride cells appeared in their stead. Under an electron microscope, vacuolation in epithelial vesicles, myelin like figures, various membrane bound vesicles and apical homogeneous layers of reduced thickness were evident. Increased amounts of particulate matter adhering to the external surface of the epithelial cells were also apparent.(35)

Zinc

As little as 0.3 ppm of zinc is toxic to some aquatic insects and 0.3 to 0.7 ppm is the toxicity range for fish.

Reproduction in the fathead minnow was almost totally inhibited at zinc concentrations that had no effect on survival, growth or maturation of these fish. At .18 ppm no effect on the survival or growth of eggs or fry was noted but 83% less eggs were produced than at a concentration of .03 ppm.(36) At sublethal concentrations of zinc goldfish behaved aberantly, failed to reproduce, had poor growth rates or functioned poorly in other respects.(37)

Thus it can be concluded that zinc is an essential element, but in fairly low concentrations it can cause serious effects not only in fish and insects but also in mammals.

Cadmium

Cadmium is extremely toxic to fish. Concentrations between .008 and .01 are lethal to 50% of a test batch of trout.(38) Concentrations of

Cd(OAc) between 25 and 50 ppm produced marked osteoporosis.(39)

In concentrations between .01 and 10 ppm the fish all overturned in a few days except in the lowest concentrations. In the upper range hyperplasia and necrosis of the epithelium of secondary gill lamellae were evident. Death probably resulted from interference in respiration.

Gill damage was less pronounced in the low concentrations. There were morphological and histological changes in the internal organs especially the spleen, which was nodular in appearance, congested and structurally changed. The liver was also affected. The heart, skeletal muscle and brain had degenerated.(28)

Tin

The 24 hr LC_{50} of stannic chloride is 78 ppm. At 46 ppm none of the fish died. Stannous sulphate failed to kill fish in 24 hours at a concentration of 553 ppm. This comparitively low toxicity in hard water is attributed to much of the material being in suspension.(28).

VI. SEDIMENT STUDY

A. Method and Results

A preliminary survey has been undertaken, by means of X-ray fluorescence, at a site on the Miami river to determine the trace element concentrations in river sediment. A second site was also surveyed, off the river, to determine if the observed analysis is for a natural or industrial origin.

The river site was chosen for its distance from any known industrial outflow so as to allow the determination of the actual background elemental load for sediment. The actual sampling position was approximately 10 miles south of Dayton, Ohio. At this point a small dam retains the river flow so that current carried particles settle and form a substantial sediment. The second site was a few hundred feet east of the Main campus of the University of Dayton. A small stream, in this area, has undercut the sides of several small hills leaving the clay substructure available for easy sampling.

The sampling technique involved taking core samples by means of a hand held coring tube. A 1-1/2 in. diameter aluminum tube was forced into the sediment and removed a quantity for sampling. A plunger was then used to remove the sample from the tube. For river sediment, vertical cores up to 30 cm. in length were taken. The clay sampling technique involved taking horizontal cores up to 30 cm. in length from the exposed side of a small hill at depths of 60, 120, and 180 cm. from the surface of the hill; the 180 cm. was just above the waterline of the stream. Samples from both sites were cut into sections, the outer portions of which were removed. This procedure was used to insure that sample contamination did not occur in handling. The cut samples were dried and ground by hand, in a mortar and pestle. The ground samples were then sifted through a screen filter which allowed particles of less than 0.048 mm. to pass. The sifted samples were then mounted in known amounts, on cellophane tape discs. Each disc was then fluoresced for 10,000 and 40,000 seconds and analysed for their trace element content. Fig. 8 shows a typical spectrum. Table 7 is the result of the procedure outlined above; the concentrations are recorded in micrograms per gram of sample.

Most sediments and all clays contain a substantial percentage of silicon, in the form of oxides and silicates;(40) it was therefore not surprising to find a large scattering background count associated with the analysis of sediment samples.(41) In an effort to increase intensities of elements contained in a sample two procedures were attempted which could possibly decrease background and concentrate the sample constituents. The first technique involved the formation of a pellet of sediment. A quantity of sediment, 500 milligrams, was placed in an aluminum die of 1/4" diameter. The sample was compressed in this mold and removed in the form of a pellet 1/4" in diameter and 1/4" in length. The pellet was mounted on a lucite rod and placed in position for analysis. The diameter of the pellet was the same as that of the collimator opening to the Si(Li) detector, and the pellet's length was assumed to be small enough to allow a fluorescence of the whole sample. This sample preparation did accomplish an over all intensity increase for the elements observed; however, it also created a proportional increase in the background. Handling of the pellets proved to be a problem due to their fragile construction and demanded much care in mounting the samples for analysis. A second procedure

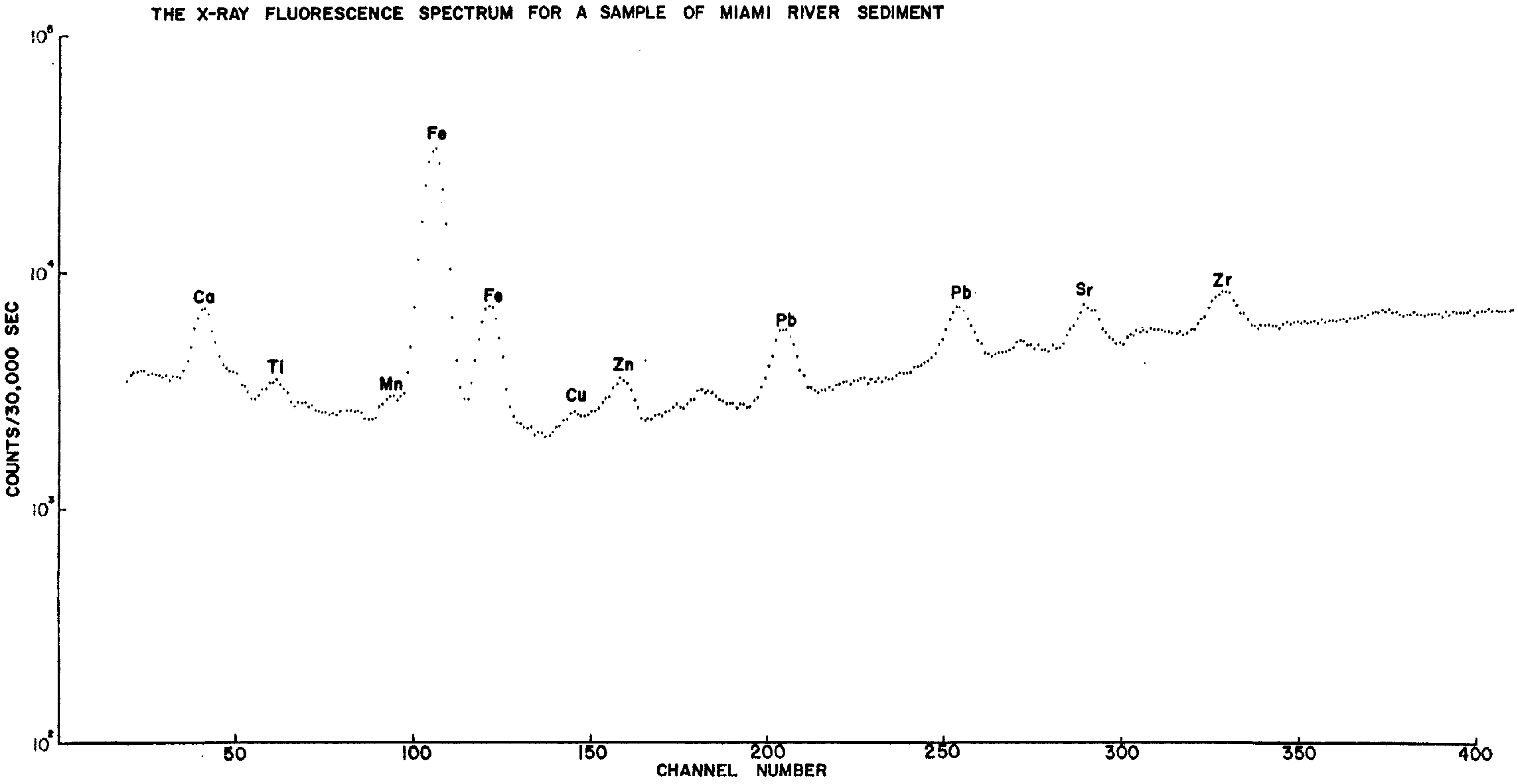


Figure 8. Typical X-ray fluorescence spectra of a sediment sample.

involved the acid leaching of a sample. A quantity of sediment was placed in a nitric acid (HNO_3) bath for 24 hours during which acid soluble compounds were ionized and went into solution, while the insoluble silicon dioxide remained unaffected. The acid solution was removed and evaporated on a mylar disc which in turn was fluoresced and analysed. This procedure was responsible for a marked decrease in background and a substantial increase in count rates. For the analysis of individual elements in known compounds, this is a very successful procedure. However, since this procedure is dependent upon the acid solubility of the compound which contains the element to be observed, the intensity increase observed varied from one element to another depending upon the solubility of the element of its compound. Table 8 represents the intensity increase observed for a given element of an acid leached sample over that observed for a sample analysed for 10,000 sec. without leaching. Table 9 represents the most likely compound an observed element is in for a sample of sediment.

Two other possible sources of trace element contaminants were also analysed for this report. A soil sample was taken for near the out flow of a sewage treatment plant and flyash from an electrical power generating plant; both sampling sites were on the Miami River and several miles above the sediment sampling site. Table 10 represents the analysis of trace element constituents of the samples; constituents are recorded in micrograms of constituent to gram of sample weight.

B. Conclusions

The analysis, by XRF, of Miami river sediment has determined the presence of 10 trace elements; 6 were quantitatively identified in concentrations of micrograms per gram of sample. Two sample sites were chosen for this survey, one on and one off the river. The sites were chosen for their apparent distance from any known industrial outflow, which could alter the trace element concentration appreciably. In this manner the trace element background level could be determined for the river sediment. Correlation of the on and off river site analyses was then used to determine a reference to the natural or industrial origin for the concentrations observed. Two possible sources of trace element contamination were also analysed for this study, soil taken from near the outflow of a sewage treatment plant and flyash from a coal burning electrical power generating station. Both positions were located on the river north of the sediment sampling site. From the analysis of all the sites the overall trace element load for the river sediment appears to be below the concentrations observed in naturally occurring clay formations.

Three procedures were established for sample preparation: pelletizing, acid leaching, and direct sample mounting. Pelletizing sediment proved to be an unsatisfactory method, by several major considerations; while the pellet did concentrate a large amount of sample, it also considerably increased the background count rate during analysis which buried small peaks. The pellet itself proved too fragile to handle without extreme care during mounting and analysis; quantitative analysis was found to be unsuccessful due to matrix absorption. Acid leaching of a quantity of sediment was very successful in decreasing background and increasing the intensities of some elements, while prepared samples could be easily handled. This preparation was found to be dependent upon the acid solubility of the compound containing the element to be analysed, which caused variations in intensity increases and made this technique unacceptable for a complete analysis. The direct mounting of a sediment sample was found to be the best preparation for analysis. A portion of a sample was dried and crushed, sifted and mounted directly to the top of cellophane double stick tape for a fast and simple technique which created a uniform, homogeneous sample of known mass which could be easily handled and analysed.

DISCUSSION & CONCLUSION

The new developments in X-ray fluorescence suggest that an analysis system capable of field operation should be developed in the near future. Also for laboratory work the best system includes X-ray excitation (with multiple secondary targets), double guard ring Si(Li) detectors and a pulsed light feedback electronics system.

The preliminary study of K_α/K_β intensity ratios has revealed some discrepancies in the literature and suggests further study. In particular the effect of sample thickness and chemical composition will be investigated.

The effect of absorption on the incoming bremsstrahlung radiation from a Pm^{147} source has been shown to be negligible. The effect of absorption on emerging radiation can be significant but can easily be corrected for. More subtle effects such as the enhancement effect require more study for metals at the ppm level. This is perhaps the only area in the X-ray fluorescence technique that requires significant research and development.

By comparing the trace element content of sediment samples at various levels from the Great Miami River with soil samples at various depths the two were similar. This indicates that the level of pollution in the river is quite low.

One of the prime areas for future studies in the trace metal area is molecule identification. That is, determining the chemical compound the metal is a part of. The method being developed in our studies now involves an area called electron spectroscopy for chemical analysis (ESCA). The technique involves ejecting the electron from a sample with X-rays and measuring the energy of the electron. This energy will be different 0.1 eV to 10 eV) for different chemical bonds allowing one to determine the metal involved in the bond.

TABLE 1

ml	weight in mg ± .2 mg	CuS peak intensity # counts
100	.9	18,267 ± 1%
250	1.6	47,522 ± .5%
500	2.9	86,539 ± .4%
750	6.0	129,043 ± .35%
1000	5.8	174,172 ± .3%

Table 1 Results involved in the verification of a linear relationship between sample thickness and peak intensity.

TABLE 2

Amount of river water poured through the sample in ml.	Width of the peak # ch. No.'s	Intensity of the peak # counts
100	18	7504 ± 91
200	18	12485 ± 116
300		19658 ± 145
500	23	35565 ± 194

Table 2 Data to accompany figure 5. Data was from the river water samples run to find the relationship between sample weight and peak intensity.

TABLE 3

The amt. of sol'n of CuS pct. poured thru the apparatus in ml.	Filter wt. in gms. ± .0001 gm.	Predicted sample wt. in gms. ± .0002 gm.	Experimental sample wt. in gms. ± .0002 gm.	% loss
100	.0967	.0015	.0009	40%
250	.0980	.0038	.0016	56%
500	.0974	.0075	.0029	61%
750	.0972	.0060	.00113	46%
1000	.0976	.0058	.00150	61%
iron filings				50%

Table 3 Data obtained from the study of wt. loss in the filtering technique.

TABLE 4

FILTER PAPER WEIGHTS
In grams $\pm$ .0002 grams

paper #	1/13/72 25°C	1/18/72 22°C	1/21/72 73°F	1/24/72 76°F	2/8/72 72°F
1	.0961	.0955	.0959	.0961	.0954
2	.0952	.0945	.0948	.0953	.0946
3	.0952	.0945		.0954	.0945
4	.0954	.0947		.0954	.0945
5	.0963	.0955			.0957

Table 4 Data obtained in the study of the weight fluctuation of the filter papers.

TABLE 5

SAMPLE WEIGHTS

In grams ± .2 mg

ml	11/18/71	11/29/71	12/2/71	12/2/71
100	.0976		.0968	.0969
250	.0996	.0993	.0989	.0989
500	.1003	.1000	.0995	.0996
750	.1034	.1027	.1024	.1026
1000	.1032	.1030	.1027	.1026

Table 5 Data obtained in the study of the weight losses in filter papers and samples.

TABLE 6

Mixture #	Pre-analysis calc. ratio	Ratio of Intensities Zn/Fe
1	4.8927	2.8365
2	4.91746	8.7402
3	10.12101	14.860
4	18.743	26.049
5	99.6576	108.406
1*	4.8927	2.7403

Table 6 Table of data resulting from the initial investigation of matrix effects using the "Scotch Tape Technique."

*implies that the mixture #1 sample was rotated 180° and reanalyzed.

TABLE 7

ELEMENT	RIVER SEDIMENT Concentration (μgm/gm)	CLAY SAMPLE (μgm/gm) 60 cm	 120 cm	 180 cm
Ca	480	<16	<16	7948
Ti	51	1667	1433	390
Mn	109	561	463	239
Fe	2106	10289	47570	26519
Co	106	248	1012	421
Ni	<10	<10	<10	<10
Cu	<10	<10	269	265
Zn	218	<10	<10	119
Sr	<10	<10	<10	<10
Zr	<10	<10	<10	<10

Table 7 Analysis of River Sediment & Clay.

TABLE 8

Ca	10x
Ti	1x
Cr	1x
Mn	1x
Fe	10x
Cu	5x
Zn	3x

1x represents the intensity observed for an element in an unleached sample.

Table 8 Intensity increase by leaching.

TABLE 9

Element	Compound	Acid Soluble(42) (yes +; no -)
Ca	$CaCO_3$	+
	CaO	+
Ti	TiO_2	-
Cr	Cr	-
	Cr_2O_3	-
Mn	MnO_2	-
Fe	FeO	+
	Fe_2O_3	+
Cu	CuO	+
	CuS	+
Zn	ZnO	+
	ZnS	+

Table 9 The most probable compound an element is in for a sample of sediment.

TABLE 10

Element	Sewage Treatment Soil (μgm/gm)	Flyash (μgm/gm)
Ca	8512	1434
Ti	453	3932
Mn	1331	<18
Fe	7864	50688
Co	<10	359
Cu	269	<10
Zn	340	<12
Sr	1195	303
Zr	1937	<10

Table 10 Trace elements in sewage treatment soil and power station flyash.

REFERENCES

1. Birks, L. S., Anal. Chem, 44, 557 (1972).
2. Phelps, P. L., Anspaugh, L. R., Koranda, J. J., and Huckabay, G. W., IEEE Trans. Nuc. Sci. 19, No. 1, 199 (1972).
3. Jaklevic, J. M., Giauque, R. D., Malone, D. F. and Searles, W. L., Lawrence Radiation Laboratory, unpublished report, LBL-10, July 1971.
4. Cothern, C. R., "Determination of Trace Metal Pollutants in Water Resources using X-ray Fluorescence," Annual Report to the Office of Water Resources Research, Department of Interior, Project Number A-019-Ohio, August, 1971.
5. Goulding, F. S., Jaklevic, J. M., Jarrett, B.V. and Landis, D. A., Lawrence Radiation Laboratory, unpublished report, LBL-9, July 1971.
6. Landis, D. A., Goulding, F. S. and Jarrett, B. V., Lawrence Radiation Laboratory, Unpublished report, LBL-320, September 1971.
7. Giauque, R. D. and Jaklevic, J. M., Lawrence Radiation Laboratory, unpublished report, LBL-204, July 1971.
8. Goulding, F. S., and Jaklevic, J. M., Quarterly Progress Report, Lawrence Berkeley Laboratory, for period Jan. 1 to March 31, 1972.
9. Palms, J. M., Wood, R. E. and Puckett, O. H., Nucl. Instr, and Met. 98, 597 (1972).
10. Zulliger, H. R., Drummond, W. E. and Middleman, L. M., IEEE Trans. Nuc. Sci. 19, No. 3,306(1972).
11. Proceedings of the International Symposium on Cadmium Telluride, a material for Gamma-ray Detectors, Strassbourg, France, 29-30 June 1971, Strasbourg, France: Centre de Recherches Nucleaires 1971.
12. Bell, R. O. and Wald, F. V., IEEE Trans. Nuc. Sci. 19, No. 3,334 (1972).

13. Cornet, A., Hage-Ali, M., Grob, J. J., Stuck, R., and Siffert, P., IEEE Trans. Nuc. Sci. 19, No. 3,358 (1972).

14. Schofield, J., Phys. Rev. 179 (1), 9(1969).

15. Wapstra, A. H., Nijgh, G. J. and Van Lieshout, R., Nuclear Spectroscopy Tables, North-Holland, Amsterdam, 1959.

16. Gilmore, F. R., Graphs of X-ray absorption Coefficients, The Rand Corporation, RM-2367-AEC, April 1959.

17. Rhodin, T. N., Ancl. Chem. 27, (12), 1857 (1955).

18. Wilson, H. N., An Approach to Chemical Analysis, Pergamon Press, New York, 1966.

19. Giauque, R. D., A. Radioisotope Source - Target Assembly for X-Ray Spectrometry, Unpublished report, University of California Radiation Laboratory, UCRL-18292.

20. Sherman, J., Spectro-chemica Acta, 7, 283 (1955).

21. Alley, B. and Myers, R., Norelco Reporter, Vol. 15, Numbers 3-4, July-Dec. 1968.

22. Adler, I., X-Ray Emission Spectroscopy in Geology, Elsevier Publishing Co., New York, 1966.

23. Mitchell, B., Anal. Chem., 32 (12), 1652 (1960).

24. Morrison, G. H., Trace Analysis; Phsical Methods, Interscience Publishers, New York, 1965.

25. Luke, C. L., Analytica Chemica Acta, 41, 237 (1968).

26. Caldwell, W. E. and King, C. B., A Brief Course in Seminmicro Qualitative Analysis, Am. Book Co., New York 3rd Edition, p. 107.

27. Guyon, J. and Jones, B., Introduction to Solution Equations, Allyn & Bacon, Boston, 1969.

28. Her Majesty's Stationary Office, Water Pollution Research (1969).

29. Schroeder, H. A., Mitchener, M. and Nason, A. P., J. Nutrotion 100, 59 (1970).

30. Mertz, W., Physiological Reviews , 49, 2 (1969).

31. Her Majesty's Stationary Office, Water Pollution Research (1968).

32. Nielsen, E. S., Marine Biology 6, 2 (1970).

33. Mount, R. and Stephan, C., J. Fishery Reserve Board of Canada, 26, 9 (1969)

34. Arthur, J. and Leonard, E., J. Fishery Reserve Board of Canada, 27 (1970).

35. Baker, J., J. Fishery Reserve Board of Canada 26 (1969).

36. Brungs, W. A., Transaction of the American Fisheries Society, 98, 2 (1969).

37. Cairn, J. and Shirer, H., Project Completion Report, Kansas Resources Research Institute, June 1968.

38. Her Majesty's Stationary Office, Water Pollution Research (1967).

39. Maehera, T., Nippon Seikeigekagakkai Zasshi (1971).

40. Tourtetot, H. A., Chemical Composition of Rock Type as Factors in our Environment, in Environmental Geochemistry in Health and Disease, ed. Cannon, H. L. and Hopps, H. C., The Geological Society of America, Nemion 123, 1971.

41. Jenkins, R. and DeVries, J. L., Practical X-Ray Spectrometry, Springer-Verlag, Eindhover, The Netherlands, 1969, pg. 134.

42. Handbook of Chemistry and Physics, Physical Constants of Inorganic Compounds, Chemical Rubber Co., Cleveland, Ohio, 1968-69, pg. 172.

ACKNOWLEDGEMENTS

We wish to thank Dr. Ken Shumate (Director) and the Water Resources Center at Ohio State University, Columbus, Ohio, for their financial assistance, advice and consideration in this project. We wish also to acknowledge financial assistance from the University of Dayton Research Council and The Research Corporation.