NBS

Technical Note 248

RADIOCHEMICAL ANALYSIS: ACTIVATION ANALYSIS, INSTRUMENTATION, RADIATION TECHNIQUES, AND RADIOISOTOPE TECHNIQUES

JULY 1963 TO JUNE 1964

EDITED BY JAMES R. DEVOE

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

THE NATIONAL BUREAU OF STANDARDS

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NATIONAL BUREAU OF STANDARDS

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ISSUED AUGUST 21, 1964

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JULY 1963 TO JUNE 1964

Edited by James R. DeVoe
Radiochemical Analysis Section
Analytical Chemistry Division
Institute for Materials Research

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FOREWORD

The Analytical Chemistry Division was established as a separate division at the National Bureau of Standards on September 1, 1963 and became part of the Institute for Materials Research in the February 1, 1964 reorganization. It consists at present of six sections encompassing some 30 different analytical competences from activation analysis and atomic absorption to vacuum fusion and x-ray spectroscopy. These competences, and in turn the sections which they comprise, are charged with research at the forefront of analysis as well as awareness of the practical sample, be it service analysis or standard reference material. In addition it is their responsibility to inform others of their efforts.

Formal publication in scientific periodicals is highly important. In addition, however, it has been my experience that informal, annual summaries of progress describing efforts of the past year can be very valuable in disseminating information. At the National Bureau of Standards such publications fit logically into the category of Technical Note. In the future we plan to issue these summaries for most, if not all, of our sections. The following is the first in this series, a report on progress of the Radiochemical Analysis Section.

In preparing this report, it has been necessary to make occasional references to existing commercial equipment. However, such mention should in no case be considered as representing a recommendation or endorsement by the National Bureau of Standards.

W. Wayne Meinke, Chief
Analytical Chemistry Division

PREFACE

This is the first of a series of annual progress reports of the Radiochemical Analysis Section of the Analytical Chemistry Division. Although this section was officially organized in November 1963 this report will cover the entire fiscal year of 1964.

There are sixteen people in this section and all except three of them--Kocol, Thompson and DeVoe--have joined us during the latter half of this fiscal year.

The purpose of this section is to develop measurement techniques for the qualitative, quantitative and structural composition of materials through the use of radioisotopes. Since the Analytical Chemistry Division is interested specifically in the characterization of very pure materials, a large portion of this section's effort is directed to the analysis of very small concentrations of the elements.

A basic requirement for the development of such measurement techniques using radioisotopes is the thorough understanding of the chemical, nuclear and physical principles which form the foundation of a new analytical measurement technique. Therefore, an effort has been made to include scientists who are oriented toward the so-called fundamental research aspects of the techniques under study. However, it is essential that the developed methods be practical in the sense that they can be used successfully on materials in which science and industry have an interest. Therefore, these developed techniques are applied to NBS standard reference materials where considerable cross checking of analytical techniques is done through the process of certification.

The section is organized into four groups: radioisotope tracer techniques, activation analysis, radiation techniques, and instrumentation.

Radioisotope tracer techniques utilize the principle that the radio-element can be detected in a chemical system by detecting its emitted radiation. To date, our principle interest has centered around the radioisotope dilution techniques, but the efforts of this group are expected to include the so-called radiometric methods as well as a variety of others.

Activation analysis needs no explanation since it has been developed to be a highly useful trace analytical method. The interests of this group are related to enhancing the effectiveness of the method either by modifying the type and energy of bombarding radiation or by utilizing a high degree of selectivity in detecting the radiation induced by bombardment.

Radiation techniques utilize the effects of the emitted radiation of a radioisotope. This group is studying the use of the Mössbauer effect for the determination of the structural configuration of trace elements in pure materials. In addition, a study of the effect of low energy nuclear recoil on chemical bonds is being made.

The instrumentation group designs, modifies, and repairs both the nuclear instrumentation and other instrumentation. A problem of ever increasing complexity is that of maintaining an adequate capability of interfacing between the various types of nuclear radiation detection equipment and a digital computer. Considerable effort is being made to maximize compatibility with a minimum of cost.

A roster of these groups is listed in Section 7.

Since the activity in radiochemistry in this Division is relatively new, much effort in the past year has been devoted to the planning and construction of facilities and instrumentation. A radiochemical laboratory which was completed in late 1963 is now being used at more than its capability of maximum utilization. A clean room has been completed this year, and is being used for the preparation of samples before activation analysis.

In approximately one year the Bureau of Standards will be moving to a new site at Gaithersburg, Maryland. Unsurpassed facilities for radiochemistry will be available. Pneumatic tube facilities are being planned for the NBS 10-megawatt heavy-water moderated nuclear reactor patterned after the Argonne CP-5, and a temporary system is being installed in the NBS 100-Mev linear electron accelerator.

Of critical importance is the problem of staffing the various groups indicated above. Efforts are being made continually, to staff the above mentioned groups with scientists in both the fundamental and practical areas so that maximum utilization of the facilities will be made as they become available.

James R. DeVoe, Chief
Radiochemical Analysis Section

TABLE OF CONTENTS

TABLE OF CONTENTS (con't)

TABLE OF CONTENTS (con't)

LIST OF FIGURES

LIST OF FIGURES (con't)

LIST OF TABLES

RADIOCHEMICAL ANALYSIS: ACTIVATION ANALYSIS, INSTRUMENTATION RADIATION TECHNIQUES, AND RADIOISOTOPE TECHNIQUES

July 1963 to June 1964

Edited by James R. DeVoe

ABSTRACT

This first summary of progress of the newly organized Radiochemical Analysis Section of the Analytical Chemistry Division at NBS covers four areas: Activation Analysis, Instrumentation, Radiation Techniques, and Radioisotope Techniques.

The present facilities including a radiochemical laboratory and a clean room facility are described and future plans for the 10 megawatt nuclear reactor and the 100 Mev Linac facilities at the new Bureau site are outlined. A teletypewriter-pulse-height analyzer interface for more efficient data handling in gamma-ray spectroscopy is described. A combination of radioisotope dilution and radiometric methods for determining trace amounts of silver and cobalt is presented. Details of a drift-free Mössbauer spectrometer which utilizes positive synchronization of a pulse-height analyzer with an electro-mechanical drive are given. Reproducible response to better than 0.5% is obtained. An apparatus for the measurement of the energy of nuclear species recoiling from clean metal surfaces in ultrahigh vacuum is described. The application of neutron activation analysis for determination of ppm levels of copper and zinc in human lung tissue is discussed.

1. FACILITIES

At present there are available to the Radiochemical Analysis Section a hot laboratory and a clean room described below, several standard laboratories for inactive work and preliminary preparations, and two counting rooms. The facilities of the Naval Research Laboratory reactor are utilized for irradiations at the present time.

A. Radiochemical Laboratory

This room, part of which is shown in Figure 1 was completed in November 1962. The Radiochemical Analysis Section has the use of four six-foot hoods and one glove box in this laboratory. These hoods are used for handling radioisotopes and for the preparation of samples for the activation analysis program. A radioactivity storage area is placed in the far corner of the room. Since this room is one of the few in the building in which radioactivity is being handled, an upper limit on the level of radioactivity that may be used is 150 Ci. In most cases only microcurie amounts of radioactivity in encapsulated sources are allowed to be removed from the laboratory. All radioactivity must be used in the hoods only.

The hoods are of the auxiliary air flow design. This means that 50% of the air exhausted through the hoods bypasses the air conditioner and enters directly above the face of the hoods. Although the summer weather in Washington is usually accompanied by high humidity there is no noticeable effect

Figure 1. Hot laboratory facility.

from the by-passed air. In winter the auxiliary air is preheated. These hoods will be moved to our new Gaithersburg facilities.

B. Clean Room

Several of the techniques in activation analysis have sensitivities which are high enough to create serious problems in handling the sample prior to irradiation. With these techniques the opportunity for introducing contaminants into the sample is very great. Even the amount of contamination by the metallic elements attached to organic dust fibers can be significant. Therefore, a room was constructed that would allow a certain amount of sample handling under controlled "clean" conditions prior to irradiation. The glove box area of the clean room is shown in Figures 2 and 3. This room was built within a preconstructed laboratory by forming and plastering a separate set of walls and ceiling inside of the existing room. The interior dimensions of the finished room are 15 x 17 feet. All corners were rounded to prevent collection of dust and Keenes' finish plaster was painted with three coats of a polyvinyl base paint. The flooring is covered with two eight-foot wide pieces of battleship linoleum so that the number of cracks in the floor is minimized.

Air is blown into the room through a pre-filter, an air conditioner, and an "absolute filter", respectively (Cambridge Filter Company, Model LA-1000). The air is exhausted through a port in the entrance door into a small anteroom where the worker puts on a lint-free synthetic fabric hat, shoes, and knee length laboratory coat. The air in the clean room is maintained at a positive pressure of 0.1 inches of water with respect to the pressure in the anteroom. An interlock system is provided in the anteroom to prevent the simultaneous opening of the entrance and exit doors.

The worker vacuums his hair and clothing with an industrial vacuum cleaner which exhausts through an absolute filter (Cambridge super-interception type) into the anteroom, dons the special clothing and enters the clean room.

Since there is a large amount of electronic equipment and radiation shielding in this room which can produce and

Figure 2. Glove box facility in clean room.

Figure 3. Another view of glove box facility in clean room.

collect dust, see Figure 4, a secondary protection of the chemical processing is used by performing the work in glove boxes inside of the clean room. Each box is provided with an interlock chamber which can be flushed with clean air before and after introducing an object into it. The glove boxes are supplied with air from a blower through an absolute filter and are maintained at a positive pressure of 0.2 - 0.5 inches of water with respect to the clean room.

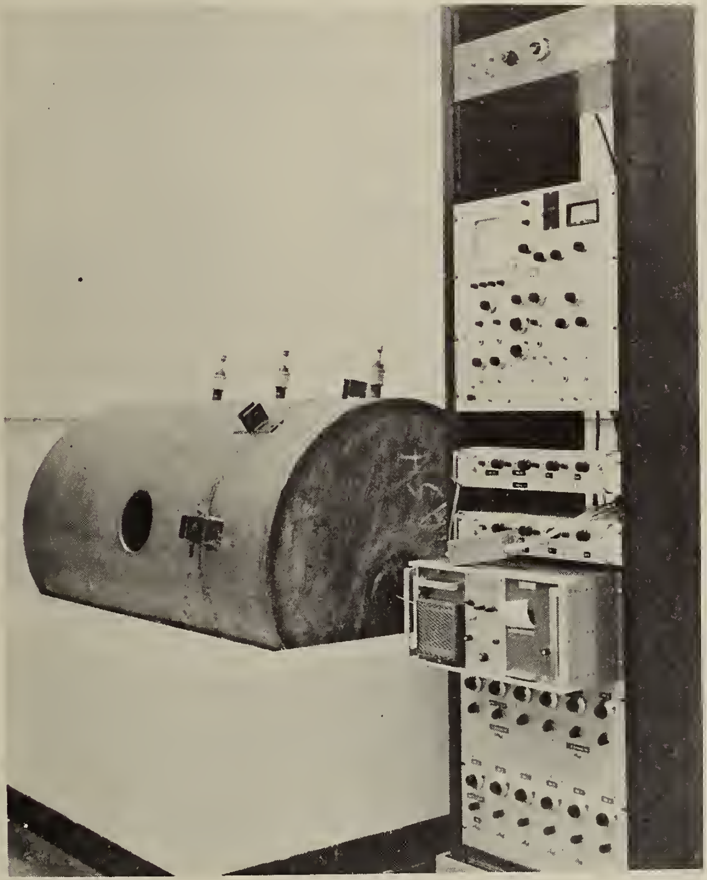


Figure 4. Another view of clean room facility.

Tests are now underway to determine the dust count in the glove boxes, clean room, and anteroom. While we believe that the particulate contamination in the clean room itself is not exceptionally low, we do expect it to be very low in the glove boxes.

Thanks are due Mr. H. Kocol for his assistance in expediting the procurement and construction of components for this clean room. The valuable assistance of Mr. B. Goetz and Mr. F. Clark is also acknowledged.

(J. R. DeVoe)

2. INSTRUMENTATION

The instrumentation used by the Radiochemical Analysis Section routinely includes a variety of α, β and γ-counting systems, several pulse-height analyzers and associated equipment such as magnetic tape, and printer readout devices.

Other equipment such as an automatic sample changer is currently being studied and tested. Our experience with it will be included in the next progress report. The design and construction of special equipment is a major part of this group's activities. The first such device is described below.

A. Interfacing of Pulse Height Analyzer to a Teletypewriter

A model 33-C ASR Teletype was obtained in order to read out the data taken by our RIDL analyzers. The teletype machine was chosen since it provided inexpensively a punch tape readout and readin as well as a printed page copy. It also offers the facility of the "Data Phone" communication.

It was necessary to interface between the instrumentation output and the teletype since the teletype would accept only a serial 8 level ASCII code and the instrumentation presented only a 4 level BCD parallel output. Provisions were made to include any arrangements necessary to read out auxilliary data from associated systems.

The interface translator unit is now operational and its performance is satisfactory. A function diagram is shown in Figure 5 and its operation is as follows:

Output data from the RIDL analyzer are fed into the input

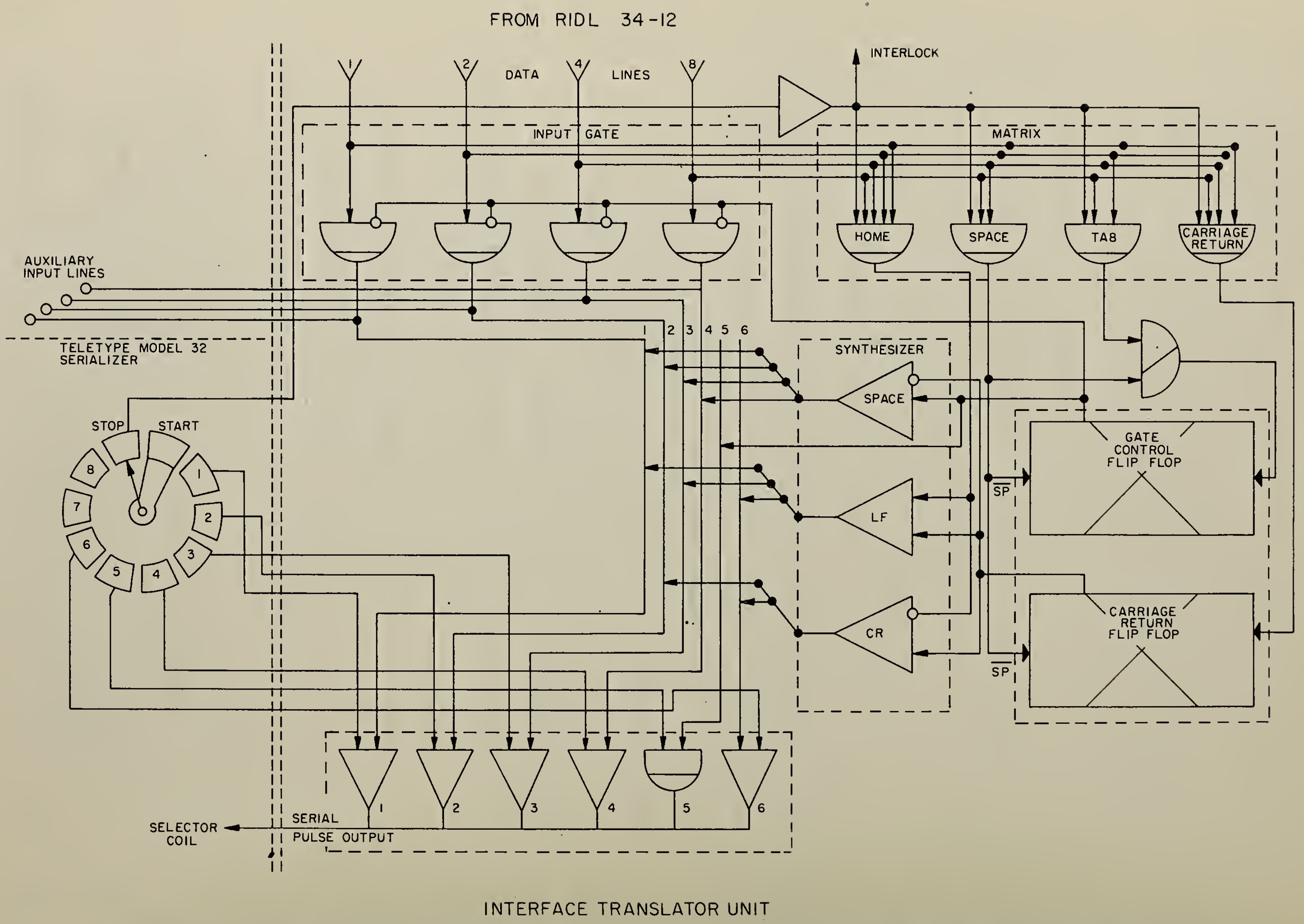


Figure 5. Functional logic diagram showing interface connecting RIDL analyzer to Model 33 Teletype.

gate and the function reader matrix. The input gate is opened for all data readout when no operation function is involved. The data are adjusted in level and then applied to the appropriate output gate inverter. When a function is called for by the analyzer, its output code is translated by the reader matrix and the data gates are turned off. A new code determined by the operation desired is generated in the function synthesizer and applied to the output gate inverters.

(R. W. Shideler)

3. RADIOISOTOPE TECHNIQUES

This group has made very significant progress in a short time in the use of radioisotopes for chemical analysis. Of particular importance is the development of the substoichiometric radioisotope dilution method for trace analysis. These techniques have been applied sucessfully to the determination of several elements in practical samples as described below.

A. Substoichiometric Radioisotope Dilution Analysis

Substoichiometric radioisotopic dilution analysis is dependent on the ability of an experimenter to manipulate a system in such a way that the same number of atoms are isolated from the bulk of the system before and after dilution. This can be accomplished in three ways: 1) Always remove the same number of atoms from solution. Solvent extraction, using a substoichiometric amount of complexing reagent in the organic phase is an example of this (see B). The analysis of silver by extraction with dithizone was accomplished in this way. 2) Always leave the same number of atoms in solution (see C). The formation of a complex with a substoichiometric amount of a sequestering reagent, such as EDTA, and the removal of the non-complexed ions by some means such as adsorption or ion exchange, is a method of obtaining the same numbers of atoms in solution before and after radioisotope dilution. The analysis of cobalt was performed by using a substoichiometric amount of EDTA and removing the free cobalt ions with a cationic exchanger. 3) To quantitatively remove all of the desired ions from solution by co-precipitation, adsorption or electroplating and then to dissolve the same number of atoms based on their solubility and/or complex formation. The latter approach has been applied to the adsorption of cobalt on manganese dioxide and to the co-precipitation of cobalt hydroxide on hydrous ferric oxide (see D).

The principle of substoichiometric radioisotopic dilution was first suggested by Ruzicka and Stary [1,2]. The following work utilizes and extends this method into a type of radiometric technique in which one need not always consider that sampling equal number of atoms of the desired element before and after radioisotope dilution is necessary. Sections B and C are abstracts of talks submitted; one to the Analytical Chemistry Division of the American Chemical Society for presentation at the fall 1964 meeting, and the other to the Symposium on Radiochemical Methods of Analysis, sponsored by the International Atomic Energy Agency, October 19-23, 1964.

(A. R. Landgrebe and L. McClendon)

B. Substoichiometric Radiometric Analysis: Determination of Trace Amounts of Silver by Solvent Extraction with Dithizone

A precise and rapid method was developed for the determination of silver in the range of 10^{-3} to 10^{-7} M. Direct isotopic dilution can be described by the equation:

$$x = y \left[\frac{A_1}{A_2} - 1 \right] \qquad (1)$$

x is the unknown and y is a known amount of the radioelement to be determined; A_1 is the specific activity of the radioisotope and A_2 is the specific activity of the mixture of radioisotope and added analyzed element. Specific activity is defined as:

$$A_1 = \frac{a_1}{m_1} \quad \text{and} \quad A_2 = \frac{a_2}{m_2}$$

where a_1 and a_2 are the activities in counts per minute (cpm) and m_1 and m_2 are the isolated amounts of the element. Since we always isolate the same amount of silver by extraction with a substoichiometric amount of dithizone, it is evident that $m_1 = m_2$. Then in relation (1) the specific activities can be replaced directly by relative activities (cpm) measured under the same conditions. This method was originally worked out by Ruzicka and Stary [1,2].

The organic phase of the system is a carbon tetrachloride solution of dithizone; the aqueous phase is a nitric acid solution of the sample. Radioisotope (Ag-110m) of high specific activity is used to determine trace concentration of the stable element through the use of a substoichiometric amount of the dithizone.

In the analysis of samples which contained large amounts of copper and trace amounts of silver it was desirable to analyze for silver without previously separating it from the bulk of the interfering ions. For silver and copper dithizonates the following expressions will hold:

$$\frac{[AgA]_{org}}{[CuA_2]_{org}} = \frac{10^8\ [Ag^+]\ [H^+]}{[Cu^{++}]\ [HA]_{org} 10^{10}} \qquad [2]$$

The charge on the elements is different and the ratio

$$[AgA]_{org} / [CuA_2]_{org}$$

depends on pH as well as on $[HA]_{org}$. In carrying out the extraction at pH 1 using a dithizone solution of 10^{-4} M at equilibrium we have for the dithizone concentration.

$$[HA]_{org} \leqslant 10^{-7} \text{ M}$$

It should be possible to extract silver in the presence of a 100 fold excess of copper at pH 1. However at pH 1, EDTA is very insoluble and we could have about 100,000 times more copper than silver in the sample we wish to analyze. Hence the determination of silver was performed at pH 4.5 in an acetate buffer, a two-fold excess of EDTA was used. At pH 4.5 it should be possible to extract all of the silver in the presence of an equivalent amount of free copper, $[Cu^{++}]$. However, in the presence of excess dithizone, both elements are extracted together. It is evident that the concentration of copper II ions in the presence of a twofold excess of EDTA is insignificant (10^{-18} M) and the copper is not extracted under the conditions employed. This method allowed the determination of silver in an NBS standard sample of Ounce Metal (85% Cu), standard sample 124d.

The method of direct isotopic dilution was quite satisfactory but it was realized that a method of double isotopic dilution is a valid means of internal standardization of the system. Analysis is carried out as follows: different but known concentrations (W_1 and W_2) of naturally occurring silver are added to two equal aliquots of the sample to be analyzed containing a concentration of silver W_x. (A ten- or twenty-fold excess compared with the amount of the element to be determined is recommended.) Equal parts of the mixture (W_x+W_2) are separated through the use of a substoichiometric amount of reagent and their relative activities are determined. The following formula is used:

$$W_x = \frac{a_2W_2 - a_1W_1}{(a_1 - a_2)} \quad .$$

a_1 and a_2 are the relative activities corresponding to the aliquots containing W_1 and W_2 respectively, after radioisotopic dilution. Maximum conditions for the use of this equation could be where $W_x = W_1$ and $W_2 \gg W_1$.

When equal number of atoms are not extracted in every experiment, a radiometric method of analysis can be used. Under similar conditions the partition function is measured by investigating the distribution of the naturally occurring silver which is traced with Ag-110^m. The silver is added to the aqueous phase and is then extracted into the organic phase with a substoichiometric amount of dithizone. This method requires the preparation of standard curves where partition function, D is plotted against the concentration of silver added. For an unknown the concentration is obtained by knowing the concentration of dithizone used and reading the corresponding concentration for a particular D from the curve. The inherent error in this approach can be minimized by preparing reference solutions which have been internally standardized by the addition of the major components that exist in the sample. The major components of the sample are present in the reference solutions in the same concentrations as would be found in the sample itself.

The analyzed copper samples (NBS Standard Sample No. 124d) were found to contain 0.021 ± 0.002% silver and this value is in good agreement with the certified value of 0.02%. The value obtained by the double isotopic dilution method, 0.025 ± 0.002% was also in good agreement. From the data obtained one may recommend the use of this radiometric solvent extraction determination of silver for the concentration range of 10^{-4} g/ml to 10^{-7} g/ml. At the higher concentrations, 10^{-4} g/ml, physico-chemical methods may be more advantageous. The sensitivity of the method is limited by three factors: a) there is a limit to which the organic reagent can be diluted because of solubility in the aqueous phase; b) the sensitivity is limited by the specific activity of the radioisotope and c) at low concentrations, silver may be adsorbed by the glass, e.g. 10^{-7} g/ml. The last factor is an error inherent in all trace analytical methods for silver.

Some uses of double isotopic dilution analysis are: 1) The method ought to be applicable to difficultly separable elements of similar chemical properties. 2) The method of double substoichiometric isotopic dilution can be used to clarify such problems as matrix effect and loss of volatile elements upon dissolution in activation analysis. 3) The technique affords considerable saving in time and cost compared to most other trace analytical methods.

(A. R. Landgrebe, L. McClendon and J. R. DeVoe)

C. Substoichiometric Radiometric Analysis: Determination of Trace Amounts of Cobalt

This analytical method is part of a general program at the National Bureau of Standards which utilizes radio-isotopic tracers for the analysis of impurities in highly purified materials. Substoichiometric radiometric analysis is a modification of the isotopic dilution method of Ruzicka and Stary [1,2]. In substoichiometric isotopic dilution analysis, equal number of atoms must be isolated from the system while in radiometric analysis the amount isolated need have only a known relation to the initial concentration. In order to isolate the same amount, or an amount proportional to the initial concentration, many side reactions such as hydrolytic reactions of the complexing agent and of the metal ion, formation of acid or basic chelate compounds other than the desired one, competing side reactions of the complexing agent with other ions present, and the reaction of metal ions with buffering and masking substances must be controlled.

Two procedures of analysis (column and batch) were developed using substoichiometric amounts of EDTA. The excess cobalt ions were removed from solution with a cationic ion exchanger in the sodium form.

Experiments were performed to determine the effect of contact time, pH, ionic strength and buffers on the sensitivity of the method. Buffering solutions investigated were sodium acetate, ammonia-ammonium chloride, trisodium phosphate and diethylamine. The method gave reproducible results with an acetate buffer for the concentration range of 10 µg/ml to 0.1 µg/ml of cobalt. With diethylamine buffer preliminary results appear to be meaningful at the nanogram/ml level. The concentration range investigated using diethylamine buffer was from 5×10^{-3} M to 5×10^{-10} M cobalt using batch experiments in which one gram of Dowex 50-X8, 20-50 mesh was equilibrated with 10 ml of aqueous solution containing a substoichiometric amount of EDTA but an amount greater than the total cobalt concentration.

Another application of this method include the measurement of specific activities of radioisotopes. Measurement of Co-60 obtained from ORNL has been done. It will be shown that substoichiometric isotopic dilution analysis is the limiting case of a more general method which is called for want of a better name, substoichiometric radiometric analysis.

(A. R. Landgrebe, L. McClendon and J. R. DeVoe)

D. The Determination of Cobalt by Desorption of Cobalt Hydroxide from Hydrous Ferric Oxide

Substoichiometric radioisotopic dilution analysis can be accomplished by quantitatively removing all of the desired ion from solution by co-precipitation or adsorption and then dissolving a constant number of atoms back into solution by utilizing their solubility and/or complex formation. This approach has been applied to the co-precipitation of cobalt hydroxide on hydrous ferric oxide.

This section presents a study of the adsorption of cobalt (II) by hydrous ferric oxide and the de-adsorption of cobalt by saturated solutions of sodium hydroxide presumably forming the species $[Co(OH)_3 \cdot H_2O]^-$ aq whose solubility would be determined by the stability constant of the complex and the solubility product of cobalt hydroxide. Cobalt hydroxide has a finite solubility. The experiments were performed to quantitatively

$$K_{sp} = [Co^{++}] \; [OH^-]^2 = 2.5 \times 10^{-16}$$

$$K = \frac{[Co(OH)_3{}^-]}{[Co(OH)_2][OH^-]} = 4 \times 10^{-11}$$

remove all the cobalt from solution and to show that the de-adsorption follows the law of mass action. The amount of cobalt adsorbed was determined by radioactive tracer methods, utilizing cobalt-60.

1. Experimental.

a. Apparatus. Automatic sample changer and scintillation counter with well type sodium iodide (Tl) crystal.

pH meter, Radiometer PHM4 (Copenhagen).

Lourdes centrifuge with maximum speed of 17.5 rpm.

Polypropylene tubes and glass counting tubes.

b. Reagents. Distilled water: prepared by passing it through a mixed ion exchange bed and distilled twice in quartz.

All chemicals used were A.R. grade.

Radioactive cobalt solutions - the cobalt-60 used was obtained from the isotope division of the Oak Ridge National Laboratory. The cobalt-60 had a specific activity of 53,650 mc/g.

c. Preliminary experiments. Cobalt nitrate (5 ml of 0.25 M) was precipitated with 5 ml of 1 N sodium hydroxide. The sample was centrifuged and the colorless supernate was decanted from the pink precipitate. To this precipitate was added 5 ml of (50%) sodium hydroxide solution and the sample was shaken for several minutes. A blue aqueous layer and a pink precipitate was obtained. It is believed that under these conditions the blue solution is collodial in nature and that the $Co(OH)_3^-$ complex is not formed as previously reported (3,4,5,6). The same results were obtained when the precipitate prepared in the manner described was equilibrated with 0.5 and 0.25 g of sodium hydroxide/ml, but with 0.125 g sodium hydroxide/ml the blue color did not form.

With (1/5) ammonia the precipitate was formed and the aqueous solution was decanted off. The blue precipitate was equilibrated with 1/5 NH_3 and an olive green aqueous phase with a blue precipitate was obtained. On standing for 24 hours the aqueous phase became amber-red indicating the formation of the ammonia cobalt complex $[Co(NH_3)_5OH]$.

d. Quantitative experiments. The data on the coprecipitation of cobalt on hydrous ferric oxide can be seen in Table 1 and Table 2. The cobalt-60 was precipitated along

Table 1. The effect of pH on the percentage of cobalt adsorbed by ferric hydroxide. [7]

Experiment A[a,b]			Experiment B[a,b]			Experiment C[a,c]		
pH	y/1-y	Adsorbed (%)	pH	y/1-y	Adsorbed (%)	pH	y/1-y	Adsorbed (%)
5.50	0.45	4.3	6.90	0.18	15.0	5.50	0.07	6.8
5.90	0.56	5.4	7.20	0.31	22.9	6.02	0.10	8.9
6.40	0.11	10.0	7.50	0.99	49.7	6.50	0.26	20.7
7.00	0.23	18.9	7.80	2.18	68.6	6.90	0.91	47.5
7.54	1.20	54.6	8.00	4.38	81.4	7.30	4.00	80.0
			8.30	5.52	84.7	7.62	10.20	91.1
						7.91	30.20	96.8
						8.20	92.20	98.9

[a] Constant factors: cobalt 2.8×10^{-9} gram atom; chloride 2.79×10^{-4} gram atoms; volume 32.1 x 0.2 ml.

[b] Fe, 4×10^{-6} gram atoms.

[c] Fe, 60×10^{-6} gram atoms.

Table 2. Effect of quantity of adsorbent, Fe. [7]

pH 6.8			pH 7.5		
Fe (g atoms x 10^6)	y/1-y	Adsorbed (%)	Fe (g atoms x 10^6)	y/1-y	Adsorbed (%)
4	0.12	10.4	4	0.81	44.7
6	0.17	14.3	6	1.20	54.7
10	0.23	18.9	8	1.48	59.8
20	0.41	27.2	10	1.67	62.6
60	0.91	47.5	20	3.44	77.5
			60	10.24	91.1

Constant factors: Cobalt 2.8×10^{-9} gram atoms; chloride 2.79×10^{-4} gram atom, volume, 32.0 ± 0.2 ml.

with iron from a solution containing 1 ml of 0.5 N ferric nitrate, 1 ml of cobalt-60 and 8 ml of 1 N sodium hydroxide. The cobalt-60 was shaken with 5 ml of saturated sodium hydroxide; the solutions were heated for several minutes at 70°C to destroy the ferric hydroxide colloid and then centrifuged. A one ml sample was counted. The remaining 4 ml of solution were filtered through millipore filters (150 microns) and a 1 ml aliquot was counted. The data appears in Table 3.

Table 3. Percent cobalt which is soluble in saturated sodium hydroxide.

cpm/ml in 5 ml of Saturated NaOH	% Solution	cpm/ml after Filtering thru Millipore Filter	% Solution
627	42.3	637	47.7
637	41.0	631	40.8
543	35.0	567	36.6
935	60.3	812	52.5
419	27.0	421	27.1

Note: If all the cobalt were desorbed in 5 ml of saturated NaOH, the concentration would be 1.550 cpm/ml.

Since the colloid was not removed from solution by the millipore filters, a method was developed to destroy any colloid formed. After co-precipitation of the cobalt with hydrous ferric oxide the precipitate was "dissolved" by shaking it vigorously. The typical reddish ferric hydroxide colloid that formed, was destroyed by heating in a water bath for several minutes until flocculations occurred. The tubes were cooled to room temperature and were centrifuged. The total volume of solution was 10 ml and contained one ml of ferric nitrate (0.5 M) which was used to co-precipitate the cobalt. One normal sodium hydroxide was used as the precipitating reagent. The specific activity of the cobalt-60 was 6 x 10^{11} cpm/g, one ml of the cobalt-60 stock solution contained 1.24 x 10^{-8} g/ml. Data for various concentrations of cobalt-60 which were de-adsorbed by saturated sodium hydroxide appears in Table 4.

Table 4. De-adsorption of cobalt from hydrous ferric oxide with concentrated alkali.

Concentration of Cobalt-60	% Cobalt in Saturated Sodium Hydroxide	Concentration of Cobalt-60	% Cobalt in Saturated Sodium Hydroxide
$4\text{x}10^{-9}$ g/ml	77.5	$1.0\text{x}10^{-4}$ g/ml	7.2
$8\text{x}10^{-9}$ g/ml	73.6	$1.5\text{x}10^{-4}$ g/ml	7.8
		$2.0\text{x}10^{-4}$ g/ml	9.3
$1.0\text{x}10^{-8}$ g/ml	90.4	$5.0\text{x}10^{-4}$ g/ml	11.3
$1.2\text{x}10^{-8}$ g/ml	64.4		
$1.6\text{x}10^{-8}$ g/ml	80.6	$1\text{x}10^{-3}$ g/ml	14.0
$2.2\text{x}10^{-8}$ g/ml	91.0	$1.5\text{x}10^{-3}$ g/ml	13.0
		$2.0\text{x}10^{-3}$ g/ml	8.3
$5\text{x}10^{-6}$ g/ml	5.1		
$1.0\text{x}10^{-5}$ g/ml	8.0		
$1.5\text{x}10^{-5}$ g/ml	7.5		
$2.0\text{x}10^{-5}$ g/ml	7.9		
$5.0\text{x}10^{-5}$ g/ml	9.7		

e. Results. Adsorption: The adsorption of cobalt-60 has been shown to follow the following expression [7,8,9]:

$$K = \frac{y}{1-y} \cdot \frac{[H_3O^+]^x}{[\text{adsorbant}]^x}$$

where y is the amount of tracer adsorbed and brackets indicates concentrations. The amount of radioactive cobalt used per sample and the total volume were known. The above equation results from treatment of the adsorption system as a cation exchange system in equilibrium which follows the law of mass action when the thermodynamic activities of the ions in solution are their molar concentrations and when their concentrations are constant. It can be seen from this equation that if the quantity of adsorbant is maintained constant, a plot of $\log \frac{y}{1-y}$ vs pH should give a straight line, likewise, if the pH is maintained constant, a plot of $\log \frac{y}{1-y}$ vs log (gram atoms of iron) should also produce a straight line. The experiment indicated that the adsorption of cobalt follows the law of mass action. The curves obtained by plotting $\log \frac{y}{1-y}$ vs pH or quantity of adsorbant are straight lines over most of the region studied. The adsorption does not follow the equation below pH 7.

De-adsorption: It was impossible to obtain meaningful results on the de-adsorption of cobalt with concentrated sodium hydroxide due to the formation of stable colloids. Other systems which shall be investigated are the co-precipitation of cobalt hydroxide with dysprosium hydroxide and gadolinium hydroxide. The adsorption of cobalt hydroxide on preformed manganese dioxide and the co-precipitation and de-adsorption of cadmium chloride on silver chloride and thallium chloride on silver chloride.

(A. R. Langrebe and L. McClendon)

4. RADIATION TECHNIQUES

A major fraction of the efforts of the radiation techniques group has in the past been directed towards instrumentation and laboratory equipment design. Now as these near completion, however, attention is being directed towards a detailed check-out of one system, the Mössbauer spectrometer, and the initial phases of data collection. The work with another system involving nuclear recoil is also presently in the data taking stage. The following paragraphs describe the equipment that has been designed.

A. Drift-free Mössbauer Spectrometer

Nuclear resonance fluorescence (Mössbauer effect) is the recoiless emission and absorption of gamma radiation by nuclei embedded in solids. The most important aspect of the Mössbauer effect is the sharply defined energy of the electromagnetic radiation, and the precise determination of extremely small energy shifts through the Doppler effect. The Mössbauer effect has many applications in nuclear physics, solid state, and more recently in chemistry. The fraction of nuclei undergoing recoiless transitions can be related to the amount of a particular isotope present in a sample. Also internal electronic and magnetic fields change the relative position of the resonances, and can be interpreted to give information about chemical structure, the nature of chemical bonding, and nuclear electric and magnetic properties. Once these shifts are measured for the various compounds, this information then can be used to identify these compounds in a sample. A study of the precision in identifying iron and iron compounds was started and a spectrometer was developed for this work.

Applications in chemistry require a precision Mössbauer (Doppler) spectrometer with enough range to include many isotopes and to obtain data in a sufficiently short period of time and in a routine manner. The availability of multichannel analyzers presented a method of conveniently obtaining Mössbauer effect data.

In previous applications, the analyzer was used as a slave unit in sorting out gamma rays as a function of the Doppler velocity. This presents several difficulties which were removed by using the analyzer to generate a digitally derived electrical signal for an electro-mechanical transducer, which produces the Doppler velocity dictated by the analyzer. This method increased the acceptable counting rate by a factor of 100 and removed possible drifts with time in the Doppler velocity calibration of the spectrometer.

A Mössbauer drive has been developed which overcomes one of the greatest difficulties that has been encountered in electro-mechanical Mössbauer spectrometers. The drive has been designed so that it can not drift with respect to position. This has been done by synchronizing the input signal to pulses from the position sensitive photocell slit system. This system starts each cycle in the same position, and hence position drifts have been eliminated.

The spectrometer can be driven in two modes: Constant acceleration and constant velocity. The constant acceleration mode input signal is obtained from the analog output of the channel advance pulses of a multichannel pulse height analyzer running as a multiscaler which generates a sawtooth wave form. The constant velocity mode input signal is obtained from a square wave which is triggered by the photocell.

Using the analog signal of the multichannel analyzer as the input to the drive, we have solved the problem of assigning an increment of velocity to a channel, because now the input voltage is proportional to the channel number and hence the velocity is a direct function of the channel number. The photocell slit system resets the address scalers before channel 399, and restarts the cycle. A distinct advantage of using the analog signal is that one does not encounter the problems involved in the D.C. stabilization of an integrator circuit such as described by Kankeleit [10].

1. Digitally Controlled Velocity

One can obtain a complete Mössbauer spectrum with a multichannel analyzer using a constant acceleration spectrometer by two methods. The first is the modulation of the pulse height by the driving wave form, and using the analyzer in the pulse height analysis mode. This method will give a good Mössbauer spectrum if the analog to digital converter is linear, but the count rate is restricted due to the long dead time required to address each pulse into the memory. The second method is to run the analyzer in a multiscaler mode and derive a constant increment of velocity for each channel. This method is far better than the first because the dead time is no longer an important factor, and the linearity requirement of the analog to digital converter is eliminated. The accuracy of the spectrum produced by this method is only as good as the synchronization between the analyzer and the spectrometer.

In the time mode, the analog signal of the address scalers has a saw tooth voltage dependence on time. Since this signal is derived from the address scalers, it is a direct function of the channel number. The synchronization between the velocity produced by the electro-mechanical drive and channel number is good to within 0.1 channel. Thus, the velocity is digitized and is made a direct function of the channel number.

The analog signal from pin 36 of plug J19 of the RIDL model 34-12 analyzer is impressed on an operational amplifier summing point which makes the output of the amplifier symmetrical with respect to ground. It is then fed into the input of the drive as shown in Figure 6. The position of the speaker at the beginning of each cycle is fixed by the photocell slit system as long as the photocell triggered pulse resets the address scalers before they count through channel 399, since the analyzer resets its own address at this point. We have found it to be a good practice to run the drive so that the address scalers are reset by at least channel 390. The address

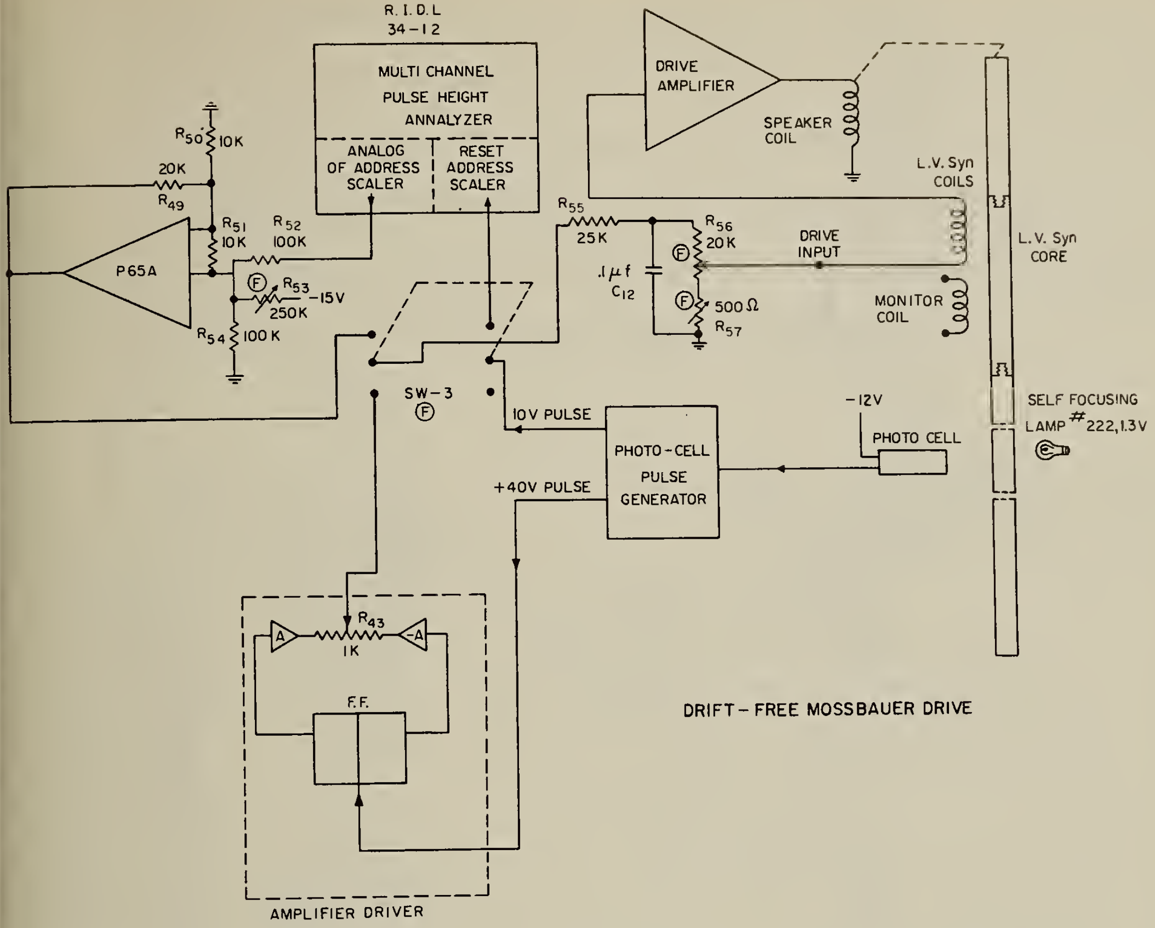


Figure 6. Block diagram of electronic circuits for constant velocity mode, or constant acceleration mode operation of the Mössbauer spectrometer.

scaler reset pulse is a -10 volt pulse derived from the photocell pulse generator as shown in Figure 7, and it is fed into the RIDL 34-12 at pin 33 of plug J2.

2. Constant Velocity

For precise stepwise scanning of a Mössbauer spectrum a constant velocity drive is very useful. The Bell Telephone Laboratories [11] drive was constructed, but due to large position drifts it was modified. The modifications in the circuit

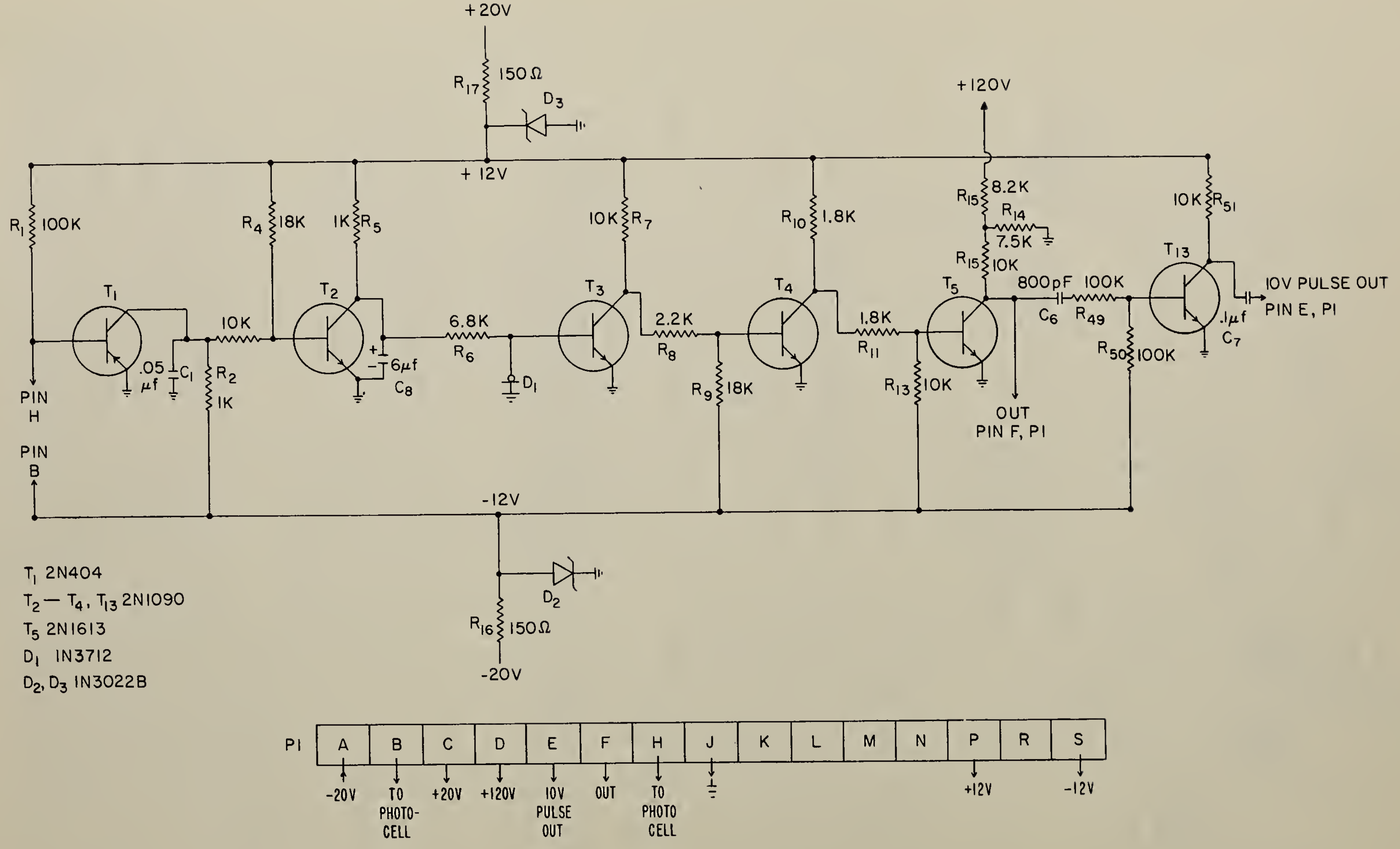


PHOTO-CELL PULSE GENERATOR

Figure 7. Circuit which generates pulse from position sensitive photocell slit system.

of the Bell Telephone drive are shown in Figure 8. The feedback system was D.C. coupled, but drifts persisted with smaller amplitudes and lower frequency. A photocell slit system was then built which generates the input square wave necessary for constant velocity as shown in Figure 6. This method of generating the square wave eliminates all position drifts.

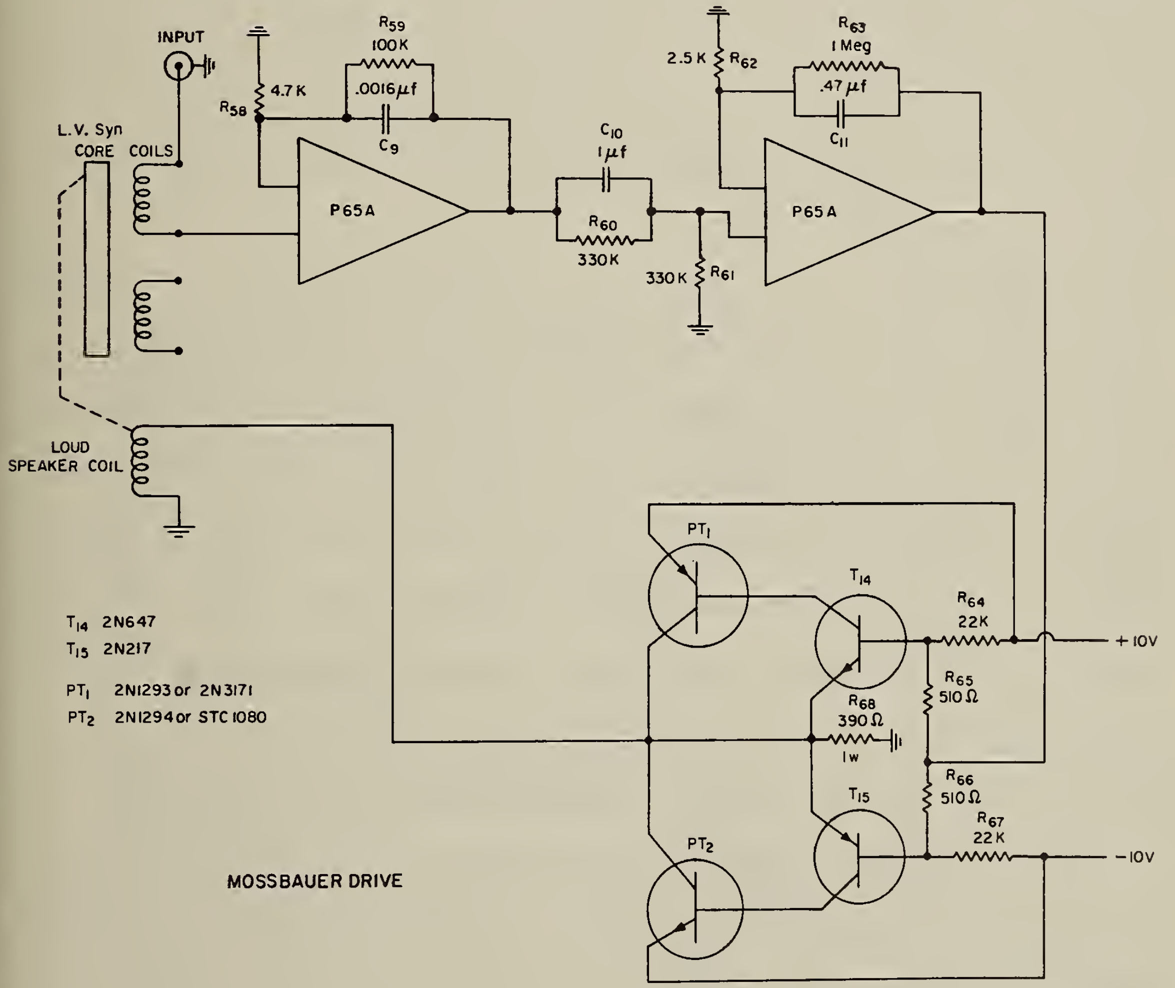


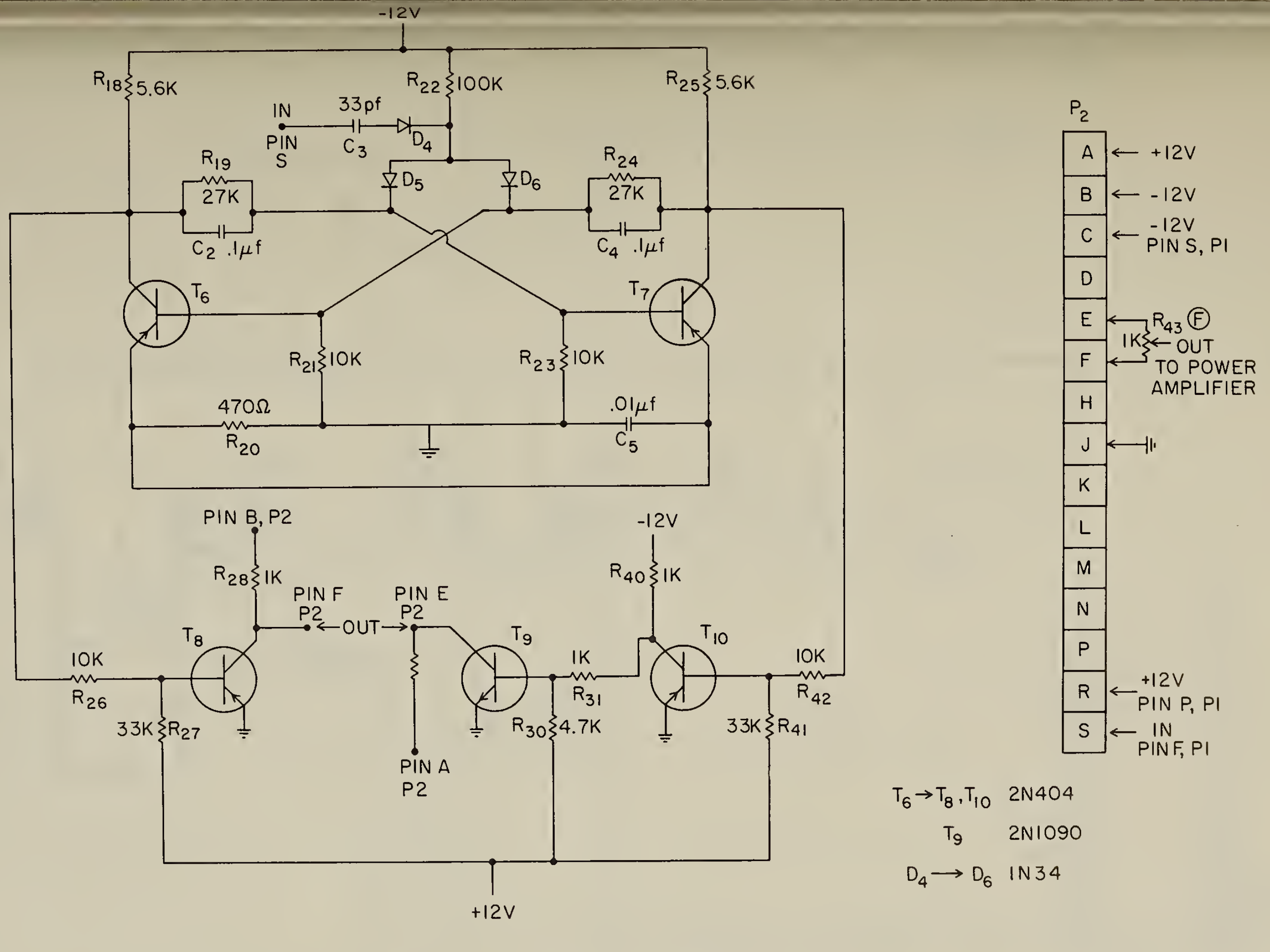
Figure 8. Circuit diagram of the modified Bell Telephone Laboratory Mössbauer drive.

A special electronic circuit described below and shown in Figure 9 was designed to generate either symmetric or non-symmetric square waves, i.e. different velocities in forward and backward directions. In the constant velocity mode, a single channel analyzer, scalers, and timers are used. We gate each scaler and timer pair on for half-a-cycle and use a time delay before they are allowed to count. This time delay allows any ringing in the turn around to be damped out and the velocity to stabilize before counting commences. Circuits for controlling RIDL models 49-43 scaler and 54-8 timer are shown in Figures 10 and 11.

3. Circuits

For simplicity the electronics for the spectrometer were divided into five circuit elements: the modified Bell Telephone Laboratory drive, the photocell pulse generator, the amplifier driver, the time delay circuits and the timer and scaler control board. They will be described below in this order.

In our spectrometer, the values for the unassigned circuit components of the Bell Laboratory drive [11] are: R=25K, C=.1 μf, R_1=20K ten turn precision potentiometer in series with a 500 ten turn precision resistor to ground. The value of C_1 was changed to 1600 pico farads to damp out oscillations that occurred in the circuit. To D.C. couple the drive a 300K resistor was placed across the 1 micro-farad capacitor, C_2. One should also note that the labeling of the power transistors in the publication in The Review of Scientific Instru-



AMPLIFIER-DRIVER

Figure 9. Circuit diagram for generating square wave input to drive in constant velocity mode.

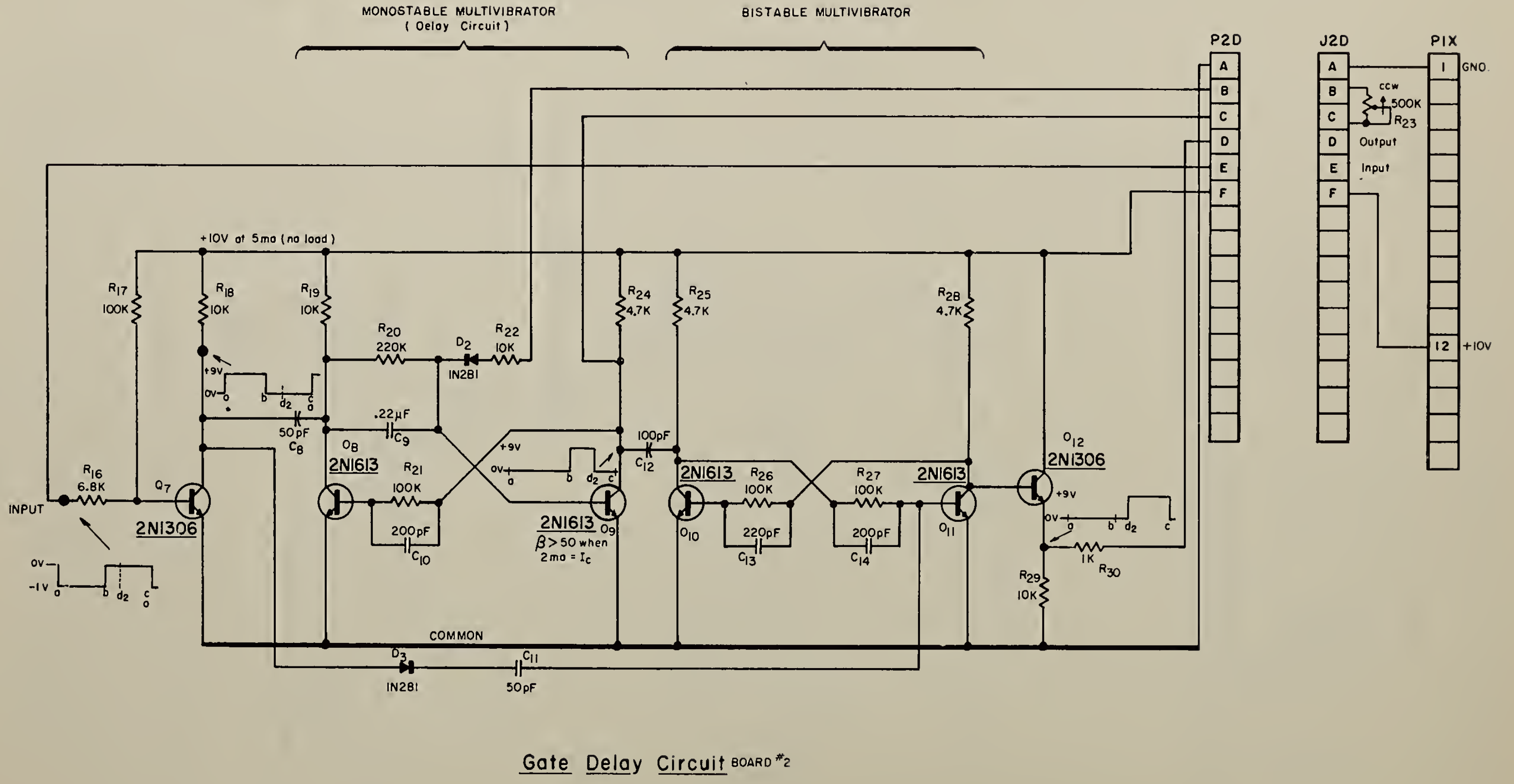


Figure 10. Circuit for generating delay pulses for controlling timer and scaler.

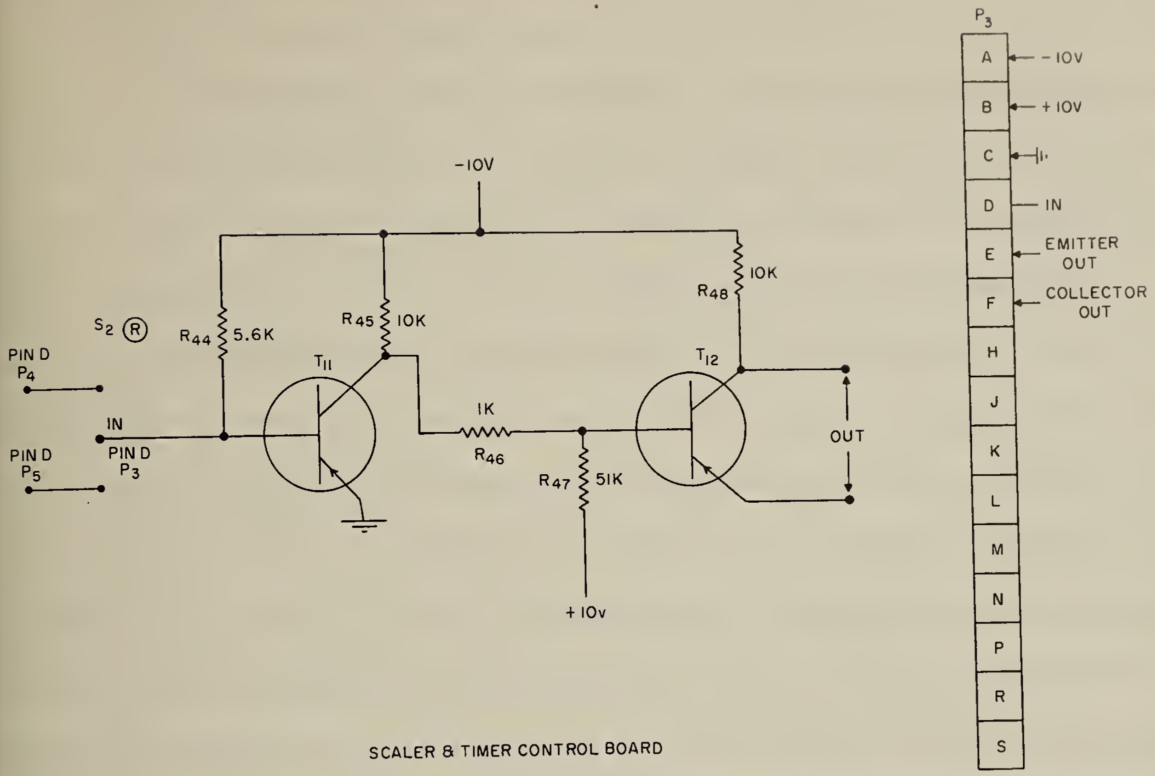


Figure 11. Interfacing between delay circuit and RIDL scalers and timers.

ments was reversed. The positioning controls R_4 and R_5 were found to be unnecessary and were deleted. To protect the power transistors from an open circuit a 390 ohm, one-watt resistor was placed from the output to ground.

The photocell pulse generator (Figure 7) uses a Clairex CL603 photocell to set the bias level for the base of transistor T_1. When the light falls on the photocell T_1 goes from a nonconducting to a conducting state. Transistor T_2 acts as an amplifier and driver for the tunnel diode trigger circuit, consisting of D_1 and T_3. The pulse is amplified by T_4 and T_5 producing a 40-volt pulse for the amplifier driver circuit. For the constant acceleration mode T_{13} produces the -10v pulse to reset the address scalers. Diodes D_2 and D_3 were added to reduce the ripple of the power supply (RIDL Model 29-1) used so that erroneous triggers caused by the ripple were eliminated.

The amplifier driver circuit (Figure 9) is a bistable [12] and three transistors, (T_8, T_9 and T_{10}). Transistor T_8 is an inverting amplifier for the output of one side of the bistables. When the T_6 is on, the output at pin F of P_2 is -10 volts, and when T_6 is off, T_8 is on in saturation, or the output is approximately grounded. Transistor T_9 and T_{10} are a cascaded noninverting amplifier which establishes a positive D.C. level. When T_7 is off the output at pin E, P_2 is approximately grounded, and when T_7 is on, the output at pin E, (P_2) is +10 volts. Now if one places a potentiometer between pins E and F of P_2, the symmetry of the voltage of the square wave can be adjusted, which is the criteria necessary to run at different velocities in the forward and backward direction in the constant velocity mode.

The time delay circuits were built by the National Bureau of Standards Electronics Instrumentation Section. These circuits provide a time delay before the timer and scaler pairs are turned on. One of the boards triggers on the positive slope, and the other triggers on the negative slope of the input square wave. Because they are very similar, only a brief description of the delay circuit (Figure 10) which triggers on the positive transition will be given.

4. Time Delay Circuit [13]

The input square wave is amplified by overdriven amplifier Q_7. The amplified signal is used to trigger other circuitry. The circuitry associated with Q_8 and Q_9 generates the delay interval. This delay circuit is a monostable multivibrator in which Q_9 is normally conducting. But when the input square wave makes its positive-going transition, Q_9 is turned off, and remains off until the end of the delay interval. When Q_9 turns on again, the negative going voltage at its collector triggers the bistable multivibrator (Q_{10} and Q_{11}) causing Q_{11} to turn off. Q_{11} remains off until the negative-going transition of the input square wave resets the bistable nultivibrator, turning Q_{11} on. Q_{12} is an emitter follower stage employed to prevent the output load from affecting the operation of the bistable multivibrator.

The timer scaler control board is an electronic switch to control the timer and scaler. The collector output is connected to pin R of the Start-Stop bistable board in scaler RIDL Model 49-43. The emitter out is connected to pin L on the same board.

The spectrometer herein described is a great improvement over previously published ones. The ideas are simple and straightforward and we believe that they are the simplest and most direct solution to many of the problems that confront workers using electro-mechanical drives. The photocell slit system can be used to control many of the drives presently in use, and instruments other than RIDL multichannel analyzers and counting equipment can be used.

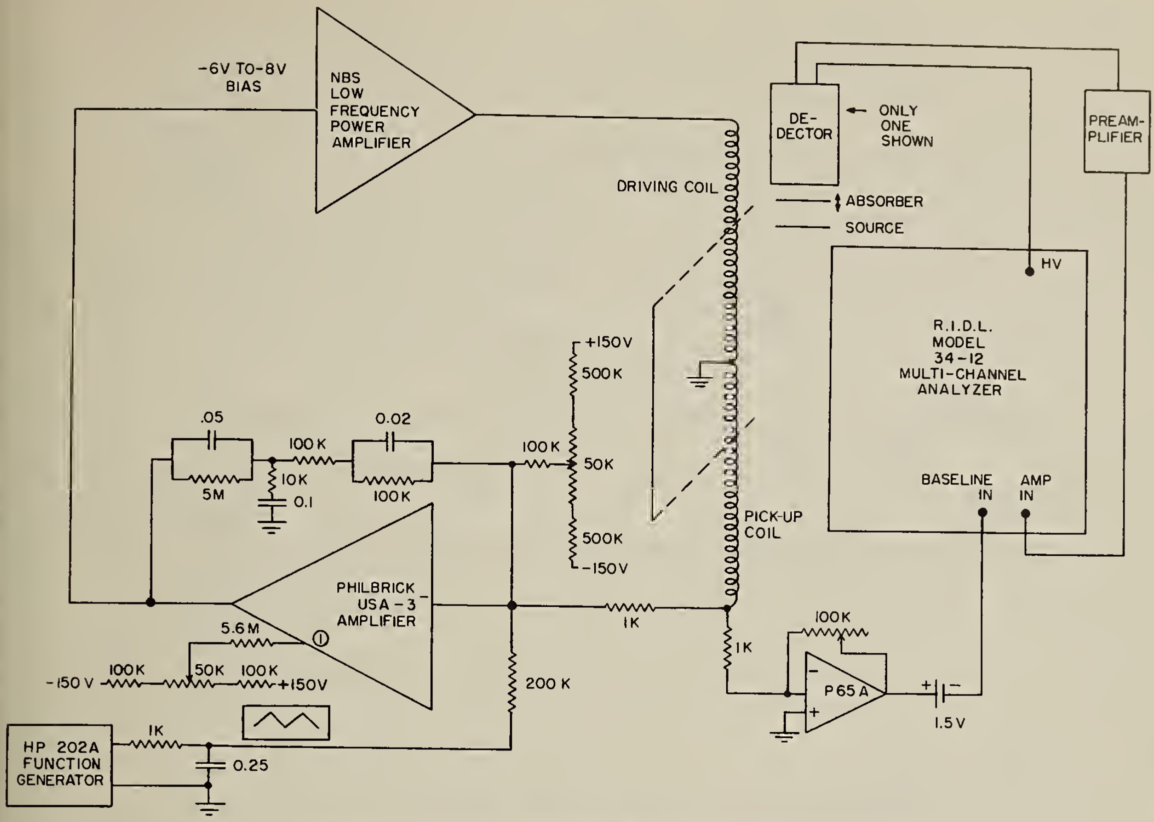
The authors would like to thank Dr. James R. DeVoe for his suggestion to use the address scalers to obtain the drive signal, and Ronald W. Shideler for his assistance and advice.

(F. C. Ruegg and J. J. Spijkerman)

B. Mössbauer Spectrometer

A Mössbauer effect spectrometer was constructed which incorporates the capability of simultaneous two system measurement with a pulse height analyzer. This instrument provides a method for calibration of an unknown Mössbauer spectrum against a standard spectrum, or simultaneous comparison of two spectra. The spectrometer is used to check the preparation of Mössbauer Co-57 sources by measuring the spectra at different periods during the anealing process to determine the degree of diffusion of Co-57 in a crystal lattice.

A diagram of the entire system is shown in Figure 12. A closed feed-back system is used which consists of a power amplifier to drive a low frequency speaker, a mechanical connection to a pickup coil which is the voice coil of another low frequency speaker, a differential input operational amplifier which drives the power amplifier to complete the electro-mechanical feed-back loop. Open loop gain vs frequency response curves indicated the proper feed-back network on the operational amplifier to obtain maximum linearity in the response of the electro-mechanical loop. The entire loop is D.C. coupled so



DOUBLE SPEAKER MOSSBAUER DRIVE CIRCUIT

Figure 12. Complete diagram of Mössbauer effect analyzer.

it is necessary to utilize a zero offset on the operation amplifier to maintain the zero signal output of the amplifier at -5 to -7 volts.

In order to minimize the 60 cycle noise in the operational amplifier a hum bucking circuit is inserted to pin 1 of the operational amplifier.

A triangular wave is introduced at the sum point of the operational amplifier. A frequency of about 2 cycles/sec was dictated by the open electro-mechanical loop response curve. Since the gain fall off began to occur at about 1 kc a maximum of about 1% linearity could be expected for a triangular wave input.

With a triangular wave input to the operational amplifier an output with parabolic shape was generated. Consequently, each half cycle contained a discontinuity at the intersection points of the parabolas. This point corresponds to the apex of the triangular wave, and a small amount of ringing was observed in the electro-mechanical loop at this point. It was found necessary to "soften" the input triangular wave at the apex by using an RC filter to cut off at 4 kc and above. This eliminated ringing in the electro-mechanical loop, but created some distortion in the motion at maximum velocity. It had no effect on the useful portion of the velocity spectrum.

A 0.0001 μfd capacitor which bypasses the collector of T1 to ground was placed in the power amplifier to eliminate a high frequency oscillation (Figure 13). The output of the pickup coil (second speaker) is amplified by the P65A amplifier and connected to the base line input of the pulse height analyzer. It is necessary to bias this signal 0 to -6 volts in order to be compatible with the base line input requirements of the analyzer.

The transducer system is shown in Figure 14. There are two low frequency response speakers that have their chassis bolted together. The diaphragm of the speaker was cut away. The spiders of both speakers are rigidly attached together with a plastic cylinder. An aluminum tube is attached at right angles to this cylinder and the absorbers are attached

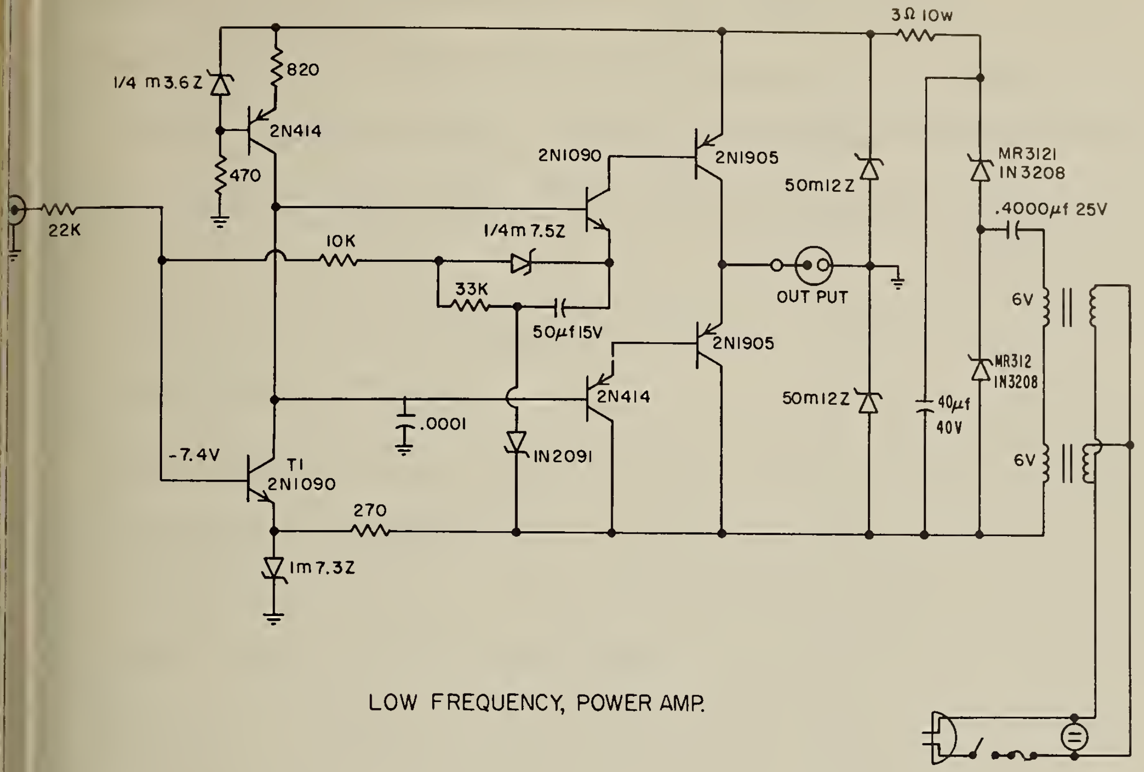


Figure 13. Low frequency, power amplifier.

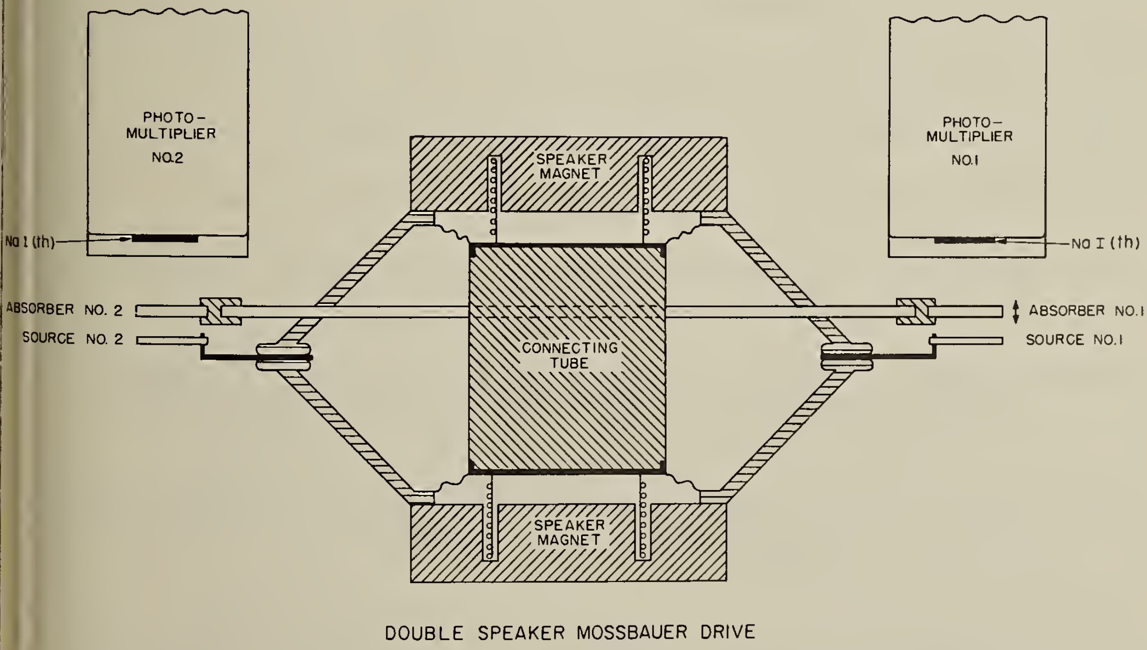


Figure 14. Double speaker Mössbauer drive.

to each end of this tube. The radiation sources are mounted to the chassis of the speakers. It is necessary to offset the position of the source from the junction plane of the speakers dince a magnetic field of about 60 gauss was found in this region.

A single detector system is shown in Figure 12. The detector-generated pulses are passed through a preamplifier, RIDL model 10-8A and into the amplifier input on the pulse height analyzer. The upper level discriminator and sensitivity control (lower level discriminator) are adjusted to allow only those pulses (e.g. energy of gamma-rays) of interest to open the linear gate to the analog digital converter in the analyzer. This constitutes a modulation of the velocity signal by the gamma-rays.

A list of the components of this system is as follows:

Hewlett Packard signal generator Model 202A

Philbrick operational amplifier Model USA-3

Philbrick operational amplifier Model P65A

Low frequency response speakers, Jenson Model P-12NF, resonance frequency 20 c/s.

Pulse height analyzer, Radiation Instrument Development Laboratories Model 34-12, modified to allow baseline input to the analog to digital converter.

Radiation detection system. Two are used, sodium iodide (Tl activated), 4 mm thick x 5 cm diameter with 0.0005" Be window.

Power amplifier. This amplifier was designed by R. J. Carpenter, National Bureau of Standards, Division 14. See Figure 13.

Preamplifier, RIDL Model 10-8A and Model 31-8A.

Mixer circuit, RIDL Model 30-17.

A disadvantage of this system is its limitation on gamma-ray count rate. High count rate produces a non-linearity in the spectrum due to the long analog to digital conversion and data storage time. The limit to the pulse rate is on the order of 5000 pulses per second.

A second detector is installed and simultaneous spectra are recorded in the analyzer by time sharing subgroups of the memory (see Figure 14). Appropriate preamplifiers (RIDL Model 31-8A) and logic circuits (RIDL Model 30-17) for the gamma-ray detectors must be used. The slow (2 μs) coincidence logic limits the overall detection efficiency of the system.

Performance of this system will be described in a subsequent report.

The author wishes to thank Dr. R. Deslattes, Section 9.5 and Dr. J. Spijkerman for their assistance in the electronic design.

(J. R. DeVoe)

C. The Use of a Nuclear Transformation to Measure the Surface Energy of Metals in Ultrahigh Vacuum

1. Introduction.

The term "hot atom" refers to an atom which has derived kinetic or potential energy as a result of having undergone a nuclear transformation. A hot atom may contain electrons in an excited state or it may be ionized, and it may have translational energy (recoil energy). It may be a stable or a radioactive nuclide. Hot atoms may be detected individually on the basis of their kinetic recoil energy, electrical charge, or radioactivity. The recoil energy available to the atom from the nuclear transformation is independent of its surroundings, and in many cases is on the order of tens of electron volts. These properties make hot atoms especially suitable for use in surface studies. In the past, radioactive atoms have been used as tracers for investigations of surface migration, sticking coefficients, and desorption energies. The availability of ultrahigh vacuum techniques makes it possible to utilize hot atoms for the direct measurement of surface energies of certain solids. The equipment described below was designed to determine the applicability of hot atom measurement techniques to the evaluation of the surface energies of chromium, cobalt, and copper.

The experimental procedure used in this work involves the preparation of an atomically clean metal surface with a high specific activity of radioactive atoms decaying by electron capture. The metal surface is prepared by thermal evaporation of the source metal onto a tungsten backing in an ultrahigh vacuum ($\sim 10^{-10}$ torr). Source atoms situated on or near the surface receive enough energy from the neutrino emission associated with electron capture to recoil from the surface. (Specifically, the recoil energy for Cr^{51} is 5.9 ev, for Co^{58}, 20.8 ev and for Cu^{64}, 23.5 ev.) After leaving the surface a fraction of the recoil atoms become ions by means of Auger electron emission. The energy of these ions may be determined by use of a repelling grid and a suitable detector. The grid potential needed to stop the most energetic ions from reaching the electron multiplier detector is a measure of the maximum kinetic energy of those ions whose recoil is vectored in the direction of the detector. This maximum kinetic energy is equal to the initial recoil energy less that needed to break free from the surface. Therefore this difference in energy is the surface binding energy.

At the time of this writing the equipment is undergoing further modification. The experience gained in the achievement of ultrahigh vacua and in the performance of the electron multiplier detector and associated circuitry will be outlined below, together with pertinent details concerning the construction of the equipment.

2. Apparatus.

a. Vacuum system. The block diagram of the vacuum system is shown in Figure 15. With the exception of the

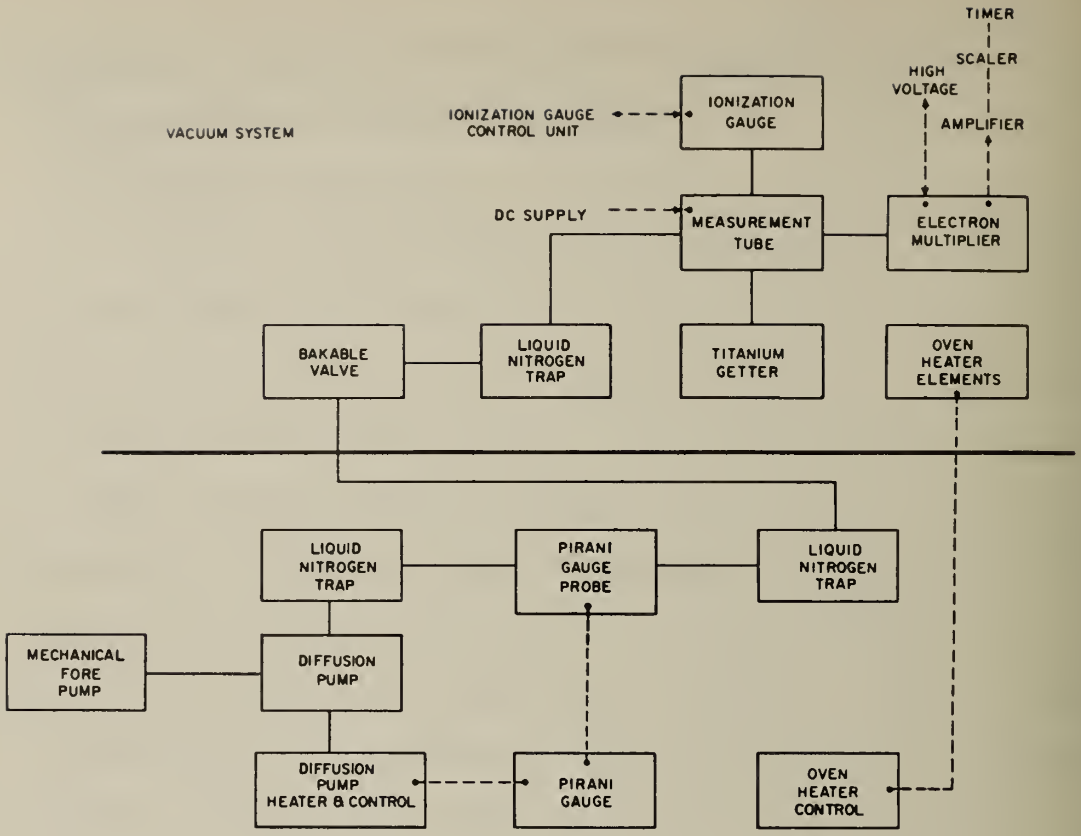
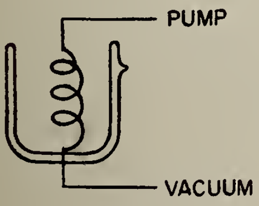


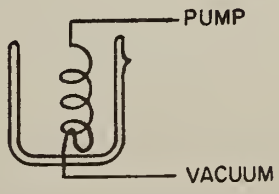
Figure 15. Block diagram of the vacuum system.

mechanical fore pump, the vacuum system was contained entirely on a wheel-mounted laboratory table 23" x 35" x 33" high. The laboratory table was modified by mounting a 1" slab of transite on the top and sheet metal across the base supports. The components of the system which were commercially available were the fore pump (Welsh Duo Seal Model 1405H), the two-stage mercury diffusion pump (Delmar Scientific Laboratory DS-7050), the Pirani Guage (CVC Model GP 105), the bakable valve (Granville-Phillips, 1/2", type C), and the ionization gauge (Varian UHV-12). The vacuum system was mounted so that the low vacuum portion (from the diffusion pump to the bakable valve) was below the surface of the table and the high vacuum portion above the table top. (The table level is indicated in the figure by the heavy line.)

The table surface served as the floor of an oven for baking out the section in which the ultrahigh vacuum is obtained. Nichrome wires were mounted on ceramic standoffs along the transite surface of the table, and their temperature controlled by means of a 30 amp variable transformer. The walls and top of the oven were formed by slabs of "Foamsil" made by Pittsburgh Corning. These slabs, 17" x 22" x 2-1/2", were wrapped in heavy duty aluminum foil which served as a heat reflector and made them easier to handle without excessive chipping or flaking. The oven temperature was monitored with a mercury thermometer (Fisher, 500°C) inserted through a hole in the oven top. Alternate layers of sheet asbestos and aluminum foil were placed below the table surface in order to cut down heat transfer to the cold traps.

The liquid nitrogen traps were used to isolate the bakable valve from the mercury vapor in the diffusion pump. The design of the trap next to the diffusion pump was adopted in order that vapors condensed on the walls of the trap would be prevented from escaping into the vacuum system as the liquid nitrogen level in the trap fell (see sketch below). The trap





MODIFIED VERSION

used in this system had a capacity of approximately two liters and appeared to work quite satisfactorily, except that on one occasion enough mercury condensed on the walls to form a drop which ran down the tubing and out of the trap. The change indicated in the right hand sketch would prevent this from occuring and preserve the good features of this trap. The second cold trap in the low vacuum line was a conventional U-bend type trap. It was packed with strips of OFHC copper which is an efficient adsorber of mercury vapor.

The titanium getter consisted of an uranium glass press with 0.030" tungsten leads and a 0.005" titanium ribbon about 0.04" wide. Current for heating the getter (and for heating the other filaments incorporated in the system) was supplied through a 6.3 volt 10 amp center-tap transformer and controlled with a variable transformer.

b. Measurement tube. A tube (see Figure 16) was constructed which would enable the kinetic energy of recoil ions to be measured. The design and construction of the grids and electrodes was done by Mr. Haliday of Division 14.02, and the glass fabrication was the work of Mr. Houck of Division 43.11. The line drawing in Figure 17 shows the main features of this tube. The sample was introduced into the system on the small tungsten filament (A) (2 mm x 1 mm x 0.025 mm) which was spot welded to 1 mm diameter tungsten rod. This filament was fitted with a quartz cap and shutter assembly (B), which served to minimize the spread of radioactivity

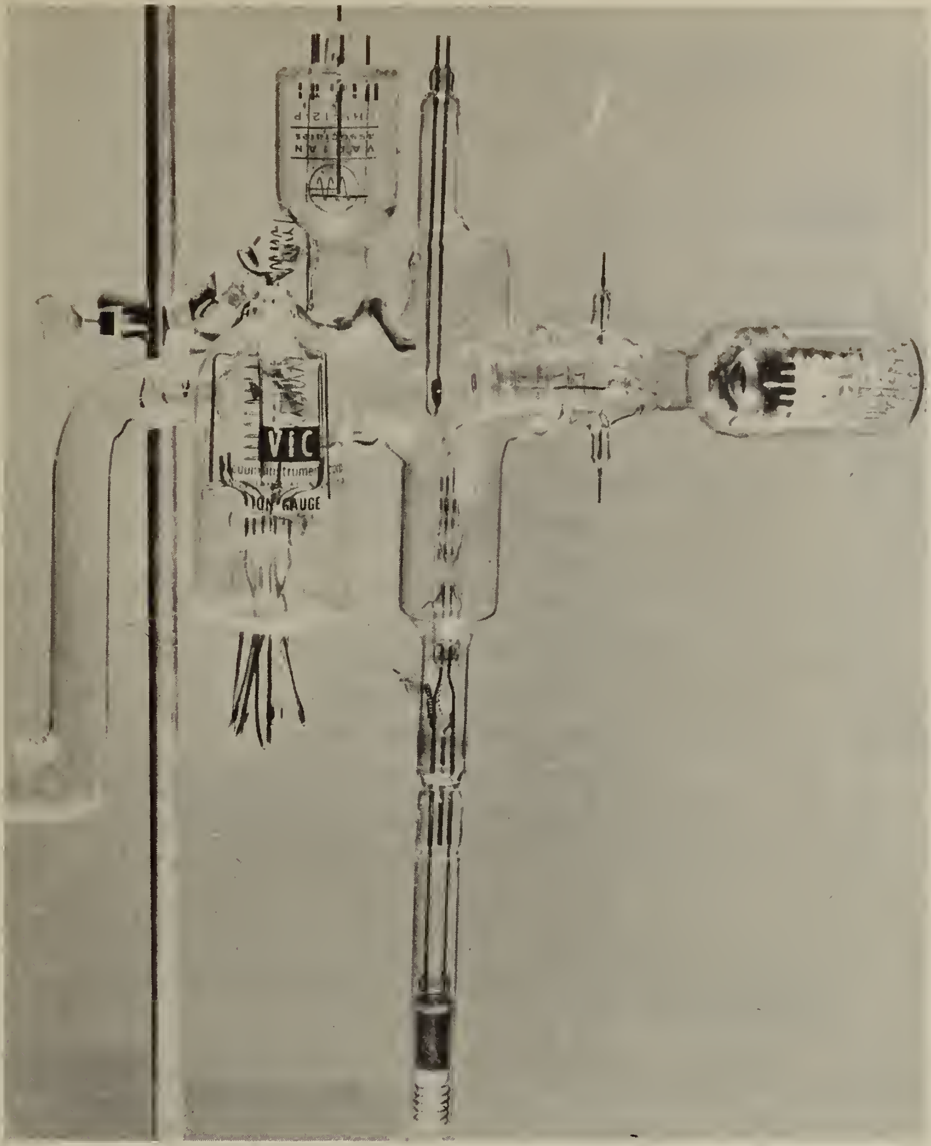


Figure 16. Ultrahigh vacuum system including tube for measurement of kinetic energy of recoil ions.

during the evaporative transfer of the source material. A 2 mm diameter hole in the cap allowed the sample to be transferred, while the quartz disc attached to the back of the cap prevented entry of the source atoms into the grid region. The small filament could be raised and lowered by means of

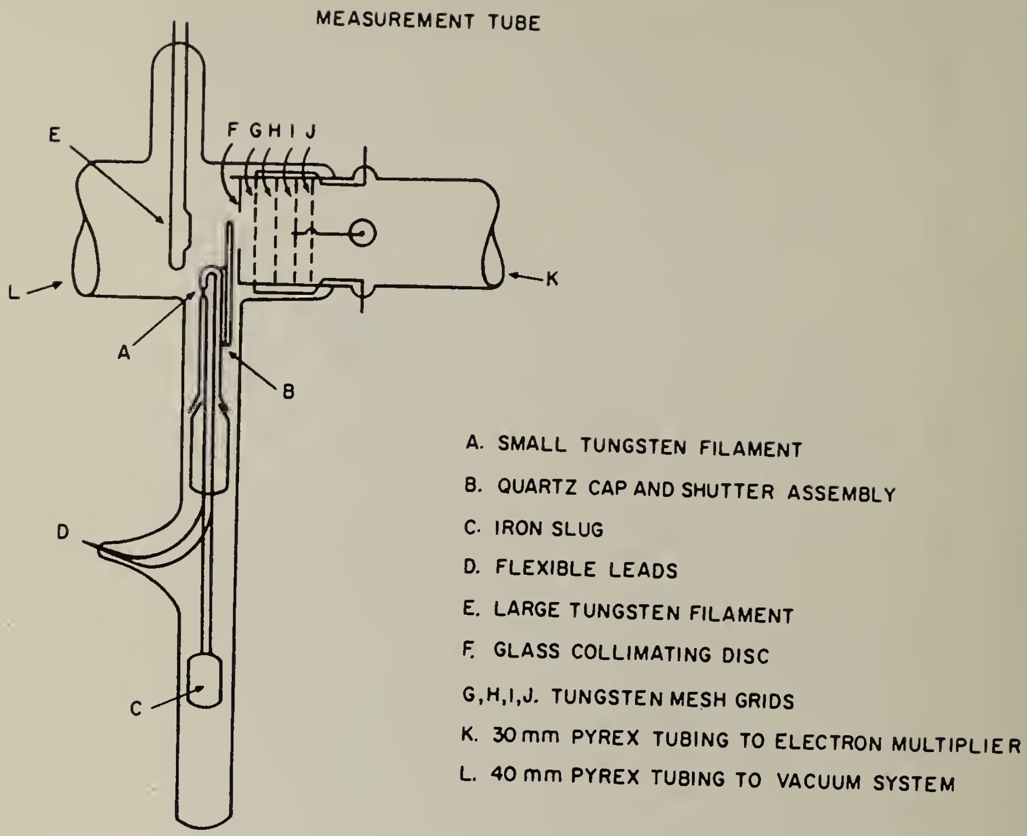


Figure 17. Tube for measurement of kinetic energy of recoil ions.

the glass-encapsulated iron slug (C) and an external magnet. The filament was heated through the flexible leads (D). After the sample was transferred to the large tungsten grid (E), the small filament and cap assembly could be lowered, thereby allowing the recoil ions to pass into the grid structure and detector. A glass collimating disc (F) with a 1 cm diameter hole served to limit the angle wherein recoil ions could approach the grids. The grids (G, H, I, J) were made from tungsten wires 0.025 mm in diameter knitted in a mesh of 32 wires per inch (available from the Metex Electronic Corporation, Clark, New Jersey). This wire mesh was sealed between uranium glass rings. The two end grids (G and J) were connected to a single tungsten lead out wire, while grids H and I had separate lead outs. The relative grid area occupied by the wire was about 6.4% for each grid, and no more than 23% for the entire system. A controlled DC potential was available for the grids by means of a 100 volt DC power supply (Electronic Measurements Company, Model TR 212A) with appropriate voltages supplied through a ten-turn helipot.

c. Detector. The recoil ions which passed through the grid structure were detected with an electron multiplier. The multiplier structure was obtained from the CBS Laboratories, and is a standard structure used in their photomultiplier tubes. It was sealed into 7052 glass tubing prepared beforehand in the NBS glassblowing shop, and had Kovar lead wires. A dropping resistor string (see Figure 18) was mounted on a Lucite tube to provide voltages for the dynodes. The switching arrangement shown in Figure 18 allowed rapid conversion of the structure from an electron detector (positive high voltage on the anode, first dynode grounded) to a positive ion detector (negative high voltage on the first dynode, anode grounded). The multiplier structure leads were attached to small clips mounted on the Lucite tube which housed the dropping resistors (see detailed sketch in Figure 18). These clips, suggested by Mr. Shideler of Section 5.01, allowed the dropping resistor string to be easily replaced.

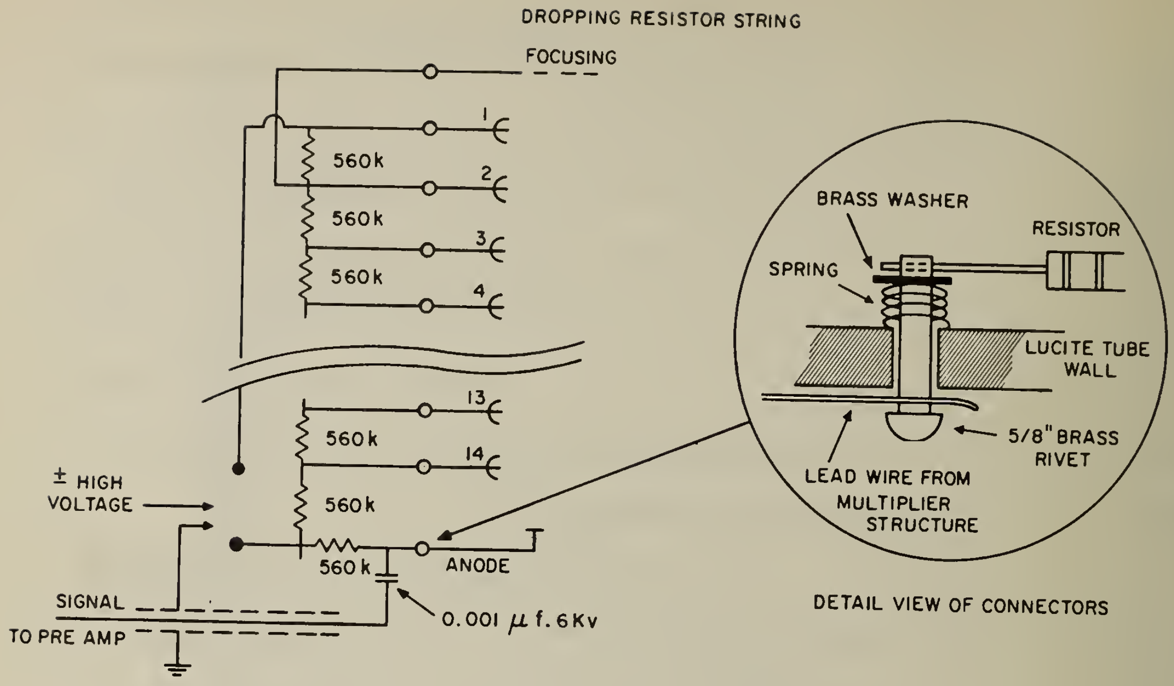


Figure 18. Circuitry associated with the electron multiplier.

Pulses generated by the multiplier structure passed from the preamplifier to an amplifier (RIDL Model 30-19) and thence to an electronic scaler (RIDL Model 40-26) with an electronic timer (RIDL Model 54-7). High voltage was provided by a 6 Kv 20 ma power supply.

3. Operating Experience.

a. Vacuum system. The vacuum system proved to be quite adequate for obtaining pressures as low as 10^{-10} torr. In only one instance during the twenty or so bakeouts performed to date was there a failure of a vacuum system component. A leak developed during bakeout in an ionization gauge-getter pump (VIC, TV-34) which was incorporated in the system as a pump. No further difficulties were encountered after this gauge was replaced with the titanium getter previously described, and the pumping performance of the getter appeared to be comparable to that of the ionization gauge-getter pump. At first the oven temperature was allowed to reach 450°C, and 500°C for short periods. It was discovered that the 7052 glass distorts under vacuum at these temperatures so the temperature was then kept in the range of 400 to 420°C. The plug which fits on the ionization gauge electrodes was found to loosen as the gauge heated during operation. This loosening resulted in spurious indications of pressure. The system functioned well after the plug was replaced by clip connectors for each gauge electrode.

The following procedure was used for baking and outgassing the vacuum system. After placing the oven over the system and filling the cold traps with liquid nitrogen, the high vacuum portion was opened to the mercury diffusion pump and the bake was started. Generally the oven temperature reached about 400°C in one hour, and was held close to this value for approximately eight hours. Then the system was allowed to cool to about 150°C and the outgassing of the ionization gauge and tungsten filaments was initiated. The ionization gauge was outgassed for one hour, and the tungsten filaments heated at bright red temperatures for shorter periods. During the outgassing the glass tubing was maintained at 120 to 160°C. On completion of the outgassing procedure the bakeable valve was closed and the ionization gauge and titanium getter turned on (the latter was maintained at bright red temperature). The pressure generally dropped to the 10^{-9} torr range within one hour, and to a low value in the 10^{-10} torr region after three or four hours. The lowest pressure obtained to date was 3×10^{-10} torr. The manufacturer reports the X-ray limit of this gauge to be 2×10^{-10} torr.

b. Measurement tube. The tube designed for measurement of surface energies was found to function well mechanically under ultrahigh vacuum conditions. The magnet (field strength about 1700 gauss) readily moved the grid and shutter assembly, and binding of glass-to-glass contacts did not prove to be a problem.

Difficulty was encountered in placing the radioactive sample on the small electrode. Several attempts were made to electroplate Cr^{51} on the tungsten electrode. This was attempted both from solutions of Cr(III) and Cr(VI). Deposition of the Cr^{51} directly on the tungsten or on a nickel-coated tugsten surface could not be achieved. The method finally adopted for placing the sample on the electrode was to concentrate the solution by evaporation under a heat lamp, and then to transfer it dropwise with a micropipette to the tungsten filament where it was evaporated to dryness. This procedure, though tedious, did allow the major fraction of the active sample to be placed on that side of the filament facing the orifice in the cap (i.e., in the best position for evaporative transfer). The same technique was used with the Co^{58} and the Cu^{64} samples.

Since the small filament holder was held in place by nickel sleeves and was readily detached from its housing, it was possible to insert the sample into the system with a minimum exposure of the vacuum apparatus to atmospheric pressure. After an ultrahigh vacuum had been obtained the system was brought to atmospheric pressure by admission of dry nitrogen. The glass tubing containing the sample filament holder was cracked off, a filament bearing the sample was inserted, and the glass resealed, again under positive pressure of dry nitrogen. The vacuum system was baked out for about four hours, and the metallic components degassed. This procedure facilitated the attainment of an ultrahigh vacuum in a relatively short time after insertion of the sample.

c. Detector. Considerable trouble was encountered because of noise in the detection system. This noise was of two types: internal noise produced by the high voltage power supply, and external RF noise from a television station and from induction furnaces operating in the area.

The high voltage power supply must be extremely quiet. In this work it was necessary to take great precautions to avoid any leakage of the high voltage through the transformers, rectifiers and other circuitry. The transformer was replaced with a "power pack" which supplied rectified high voltage (controlled by a variable transformer on the input side) directly to the series tetrode of the supply. This arrangement eliminated the high voltage noise problem.

The external noise pick-up was thought to be caused by inadequate shielding of the detector. The preamplifier was removed from its chassis and mounted on the Lucite tube that housed the dropping resistors. A thin-walled copper cylinder was placed over the multiplier and resistor structures, and this cylinder grounded to the shielded cable of the signal lead going to the amplifier. This shield also served as the reference of the high voltage. These modifications eliminated pick-up of the television signal, but did not solve the problem of noise generated by induction furnaces. Since it appeared that elimination of this noise would require considerable effort, such as the construction of a Faraday cage, it was decided to schedule the experimental work at times when there was minimum likelihood of interference from the induction furnaces.

The original detector was a ten stage electron multiplier. This multiplier proved unsatisfactory for this application because the internal noise generated a rather high background counting rate. In order to get millivolt amplitude pulses from the detector-preamplifier combination it was necessary to have a voltage drop of about 4000 volts across the multiplier. Since the multiplier structure was designed to operate at no more than about 150 volts per stage, noisy operation at very high voltages was understandable. The ten stage multiplier structure was replaced with a fourteen stage one from the same manufacturer. This new detector gave millivolt output pulses with a 2000 volt drop across the multiplier structure and had a low background counting rate. No deterioration in either multiplier's performance was noted as a result of repeated opening and baking out of the vacuum system.

(J. Thompson)

5. ACTIVATION ANALYSIS

The activation analysis group is in the early stages of development, and much effort has been directed towards plans for new facilities at the NBS Reactor and the Linear Accelerator. Some work, however, is being started on analysis of special standard reference material. During the past nine months one detailed effort in this area has been undertaken by a visiting scientist from the U. S. Public Health Service, Robert Keenan. His work involves a study of trace element analysis in human lung by neutron activation. A preliminary discussion of this work is given below.

A. Activation Analysis of Human Lung Samples

The primary purpose of this phase of the project is the development and application of rapid one- or two-step radiochemical procedures for the separation of desired radionuclides, which are produced in biological samples by short irradiations with thermal neutrons and which are determined subsequently by gamma-ray spectrometric analysis of the separated fractions. A further objective is the evaluation of chemical yield factors which are established from consistent recoveries of the radionuclides in standard samples irradiated along with the biological samples. The yields are estimated by comparing the gamma-ray spectra of aliquots of the standard samples, carried through the separation procedures, with those of other aliquots of the same standards counted directly with the spectrometer. Throughout this work, efforts are made to define the optimal conditions of each experimental procedure so as to provide the most consistent analyses consonant with conveniently executed laboratory techniques.

Ion exchange and liquid-liquid solvent extraction systems are utilized to provide rapid, clean separations of the desired radionuclides from sodium, present in part per thousand concentrations, and from one another, in part per million levels. These separation procedures are applied to solutions of the ashed biological samples. As there is a two-hour interval from the end of the irradiation to the time of dissolution of the ashed samples, the separation procedures must be sufficiently rapid to permit the completion of the gamma-ray analyses within the subsequent three- to four-hour period and thus provide enough activity for valid counting of such radionuclides as copper-64 and manganese-56.

A supply of human lung samples from adult subjects, ranging up to 107 years of age, is available as the source of experimental material. These samples have been preserved in 10% formalin from the time of collection. Since lungs are the target organs in exposures to atmospheric contaminants they should contain most of the trace elements to be found in the human organism. Hence, lung tissue is a most appropriate biologic material for activation analysis procedures.

Since the reliability and the precision of activation analyses exceed those of other methods commonly employed for the development of analytical data on biological materials, the careful application of the procedures devised and used in this project may help to reduce some of the disparities observed among reported trace element data for adult human lung tissue.

1. Instrumentation.

An RIDL, Model 34-12, 400-channel transistorized spectrum analyzer has been used for most of the analyses performed on this project. Auxiliary components include a Harshaw Type 20, MBWS, 16/5 B-X, 5" x 4" sodium iodide (thallium-activated) crystal with an aluminum well 7/8" I.D. x 2" deep. The crystal is mounted in a stainless steel container and is coupled with a 5" multiplier phototube RCA 8055 with an external magnetic shield. This crystal assembly is used in a custom-built shield containing 3" thickness of mercury metal.

2. Preparation Procedures.

a. Standard solutions. The first standard solutions for this project were prepared from C.P. reagent grade chemicals However, these were not sufficiently pure as evidenced by the appearance of a small photopeak for sodium-24 at 1.38 Mev in the gamma-ray spectra of the manganese and zinc standard solutions after irradiation for 30 minutes with a thermal flux of 10^{13} n cm^{-2} sec^{-1}. Spec-pure reagents manufactured by Johnson, Mathey and Company, Ltd., London, England and supplied by Jarrell-Ash Company, Newtonville, Massachusetts were then used to prepare each standard solution. The oxides and salts used for this purpose were CuO, $MnCO_3$, ZnO, Co_3O_4, NiO, $SrCO_3$, and

CdO and the following solutions were made up in 1% HNO_3 to provide separate standards with the stated element concentration per 100λ of solution: Mn B:0.5 µg; Mn C:0.1 µg; Cu B: 2.5 µg; Cu C:0.5 µg; Zn B:50.0 µg; and Zn C:10.0 µg.

b. Reagents. HNO_3, concentrated: A 2-liter quantity of this reagent was redistilled in an all-borosilicate glass still.

HNO_3, 1%: Prepared, as needed, by dilution of the concentrated HNO_3 with distilled water.

Extraction dithizone solution: A 100-mg quantity of dithizone was dissolved in CCl_4, A.C.S. grade, and made up to 500 ml.

Acetate buffer: Equal volumes of 2 M $NaC_2H_3O_2 \cdot 3H_2O$ and 2 M CH_3COOH were mixed.

Hydrochloric acid, 5 M, 3 M, 0.02 M, and 0.001 M: Prepared, as needed, from the C.P. concentrated reagent by dilution with distilled water.

Chloroform: A.C.S. grade, suitable for use with dithizone.

Carbon tetrachloride: A.C.S. grade, suitable for use with dithizone.

Acetylacetone: Reagent grade, B.P. range 135-140°C.

Diphenyl thiocarbazone (dithizone): A.C.S. grade.

Anion exchange resin, Dowex 1-X8, 20-50 mesh, chloride form: Each batch was equilibrated in 3 M HCl for 24 hours and then washed with distilled water until neutral to alkacid test paper

Fe, Zn, and Cu carrier: Prepared to contain 320 µg Fe^{+3}. 25 µg Zn^{+2}, and 1.25 µg Cu^{+2} per ml of 5 M HCl.

c. Collection of human lung samples. Each sample, consisting of a single piece of tissue, was preserved in a 10% buffered formalin solution in a separate, screw-cap jar for a period of 1-1/2 to 2 years. Before use, the new jars were chemically cleaned with chromic acid solution and concentrated nitric acid, filled twice with tap water to remove the acid fumes, and then rinsed 4 times with single - and then double-distilled water. The plastic caps were washed with a detergent solution, rinsed thoroughly with water, and dried in an oven along with the jars. The cleaning of the jars and the preparation of a single, 20-liter batch of formalin were performed in the project leader's laboratory at the Occupational Health Research and Training Facility, PHS, Cincinnati, Ohio. A supply of the jars and a 4-liter portion of the formalin were sent periodically to the pathologist who supplied the samples. The request to the pathologist specified the following desired conditions to be observed in collecting the specimens:

1) Insofar as possible, obtain lung specimens from 100 consecutive autopsies of subjects over 21 years of age so as to exclude those outside the adult population.
2) Take the sample from the lingula portion of the left upper lung as this is frequently the site for surgical lung biopsy.
3) Use care in handling the samples and avoid contact

with possible contaminants as the samples would be analyzed for heavy metals.

4) Use the jars and the formalin provided.

5) Provide the information requested on the label, i.e. hospital number, age, sex, and race.

d. Drying and grinding of human lung samples. The lung samples were removed from their containers, rinsed with distilled water, and then blotted and squeezed gently between several layers of filter paper to remove the excess moisture. The wet weight of the samples, contained in separate, weighed 250-ml Griffin beakers, were obtained with a Mettler balance. The samples were then dried in a vacuum oven operating at 55-58°C and 400-600 torr. A period of 3-5 days was required for the drying of a group of 8-9 samples to constant weight by this method.

When drying was complete, the beakers containing the samples were placed on clean paper toweling on the bench to cool and to permit equilibration of the containers with the laboratory atmosphere for a period of 1 hour. The dry weights of the samples were then obtained.

The samples were transferred to separate, chemically clean, 60 ml, Clearsite (polystyrene) plastic vials. A 3/8-inch Plexiglass (methacrylate) ball was placed in each vial which was then capped with a polyethylene cover. The samples were shaken for exactly 10 minutes in a Spex Industries Incorporated Model 8000 Mixer/Mill. At the end of this period the sample appeared to be finely ground. The ground samples have been stored in their respective vials since grinding.

e. Preparation of encapsulated samples for irradiation. A supply of 3/4- and 1-1/4-inch lengths of Intramedic polyethylene tubing, medical formulation PHF, .320" I.D. x .364" O.D., Catalog No. PE430, Clay-Adams, New York was cut and soaked in redistilled concentrated nitric acid for several hours. (Initially, the cut lengths of tubing were immersed in aqua regia but this was discontinued after it was found that leaching with nitric acid resulted in a reduced activity of the polyethylene capsules after irradiation.) The tubes were then rinsed with several portions of distilled water and submerged in several changes of distilled water over a period of 24 hours. They were rinsed with 2 portions of C.P. acetone, air-dried, and one end of each tube was flame-sealed.

Each 3/4-inch tube was loaded with a 100λ volume of the appropriate standard solution in 1% nitric acid medium. Two standard solutions of a given element were prepared with the concentrations of this element so chosen that the anticipated quantities of the same element in the "unknown" lung samples would be bracketed. The remaining open end of each standard capsule was flame-sealed immediately after the introduction of the solution.

Each 1-1/4-inch tube was loaded with a 125-milligram quantity of a dried, ground lung sample. The open end was flame-sealed carefully. All sealed capsules were then submerged in redistilled, concentrated nitric acid for 2-3 hours and then rinsed and leached with distilled water as described above. After rinsing twice with acetone and air-drying, they were transferred to several layers of paper tissues and taken to the reactor site, without touching with the hands.

3. Irradiation Procedure.

The encapsulated samples and standards were placed in a polyethylene rabbit which was introduced into Glory Tube No. 2 at the Naval Research Laboratory's research reactor. By means of a length of twine, the rabbit was allowed to drop to a point which was 13 inches from the bottom of the front face of the core of the reactor. All irradiations to date have been conducted for exactly 30 minutes with a 5-minute cooling period.

4. Radiochemical Procedures

a. Ashing method. The capsules containing the samples are cut open with scissors and the irradiated lung samples are shaken into chemically clean, 20 ml Griffin beakers. After the addition of 1-2 ml of concentrated nitric acid the samples are evaporated on a low temperature hotplate (ca 130°C) nearly to dryness. After the addition of another 1-2 ml of the acid, the beakers are covered with clean watch-glasses and heating is continued. The samples are subjected to this treatment and to alternate, brief heating at the highest temperature obtained with the hotplate until ashing is complete as evidenced by the production of a white or very light colored residue.

The sample is then treated twice with 10-12 drops of concentrated HCl and evaporated just to dryness on the low temperature hotplate. This latter step serves a twofold purpose - complete dissolution of the residue demonstrates that ashing is complete and the double evaporation with the acid is helpful in converting any pyrophosphosphate to orthphosphate. Pyrophosphate, formed during the high temperatures reached in ashing procedures, will complex certain metallic elements thus rendering them ionically unavailable for subsequent ion exchange separations or reaction with chelating agents.

The residue resulting from the hydrochloric acid treatment is dissolved in 2 ml 5 M HCl. The sample is now ready for either the ion exchange separation procedure or for one of the solvent extraction methods.

b. Treatment of standard samples. The 10 and 50 μg zinc standard samples subjected, along with 4 lung samples, to the first irradiation on this project were transferred to tubes and counted directly. The resulting standardization factors of 133 and 135 cpm per μg Zn showed remarkably good agreement. This high degree of precision was also obtained with other zinc standards in subsequent irradiations.

The copper and manganese standards irradiated on January 23, 1964, along with 4 lung samples, were carried through the same ion exchange separation procedure as that applied to the ashed lung samples. Due to the poor agreement in the two values of the standardization factors obtained for both copper and manganese, it was decided that in subsequent runs it would be advisable to split the standards after irradiation and to count one-half of each standard directly and to carry the other half through the radiochemical separation procedure. By this approach it was hoped that (a) this would serve as an independent check on the actual amount of radioactivity contained in each standard, by reason of the direct count; (b) this would provide a means of estimating the chemical yield applicable to the lung samples carried through the same separation procedure; and (c) the monitoring of the thermal neutron flux inside the rabbit by means of the standard samples would still be accomplished.

From the date of the third irradiation through the eighth, the standard samples have been split after transfer from their capsules to separate beakers. The transferred solutions are acidified, evaporated just to dryness, dissolved in 2 ml 5 <u>M</u> HCl and measured aliquots taken for the direct count and for the application of the radiochemical separation method.

c. <u>Ion exchange separation method</u>. An extensive amount of experimentation has been directed towards the evaluation of the optimal conditions for the separation and elution of certain metallic elements, including zinc, copper, and cadmium, which form chloro complexes and, as such, are adsorbed by an anion exchange resin. It was found that the final exchange procedure used on this project provided complete separation of these three heavy metals present in 125 mg of dried lung in a total quantity less than 0.5 µCi, from a calculated 0.4 mCi of sodium-24 and 1.0 µCi of manganese-56. The variables studied in this experimentation included (a) the mesh size of Dowex 1-X8, (b) column length with a fixed diameter of 0.6 cm, (c) flow rate, and (d) molarity of HCl for elution of separate metallic constituents. The final conditions selected as the result of these studies are presented in the following procedure.

The ashed lung sample, containing 1000 µg carrier Zn and 50 µg carrier Cu, but no holdback carrier, is dissolved in 2 ml of 5 M HCl. This solution is added to a 3 cm column of Dowex 1-X8, 20-50 mesh, supported on a small pad of Pyrex glass wool in a 0.6 cm glass chromatographic tube prepared from soft glass tubing. The lower end of the tube is constricted and fitted with a short piece of Tygon tubing and a screw clamp to adjust the liquid flow to one drop per 4 seconds. The effluent and the three, 2 ml 5 M HCl eluates are combined and may be analyzed for manganese-56 after separating this radionuclide with acetylacetone using chloroform as extractant. The copper is eluted from the column with four, successive 2 ml volumes of 3 M HCl and these separate eluates are analyzed by gamma-ray spectrometry. Zinc is eluted with five, successive 2 ml volumes of 0.02 M HCl which are likewise analyzed. Split standard samples of Zn and Cu, irradiated at the same time as the "unknowns" are carried through the ion exchange separation procedure simultaneously, and the chemical yield of each of these radionuclides is estimated by comparison with the gamma-ray spectrometric analyses of the other aliquots of these samples which were counted directly. The chemical yield of zinc-69m obtained for the analyzed portions of a set of zinc standards was determined to be 48% on the basis of the data from Irradiation No. 3 presented in Table 5.

Table 5. Analytical data on a pair of irradiated and aliquoted zinc standard samples (using peak height measurements of recorded 0.438 Mev photopeak of Zn-69m).

Standard	µg Zn in Aliquot	Treatment of Aliquot	Total CPM	Std. Factor (cpm/µg)	Chemical Yield (%)
Zn B	25	Direct Analysis	690	27.6	--
Zn C	5	" "	145	29.0	--
Zn B'	25	Ion Exchange	308	--	44.7 ± 10.4%*
Zn C'	5	" "	73	--	50.4 ± 10.4%*

*Errors are standard deviations of eight determinations.

The standard deviation of ± 10.4% shown in this table for the chemical yield values is based upon the experimental work performed during the evaluation of the optimal quantity of carrier zinc. This value is possibly larger than that which would be obtained from a repetitive series of recoveries with the final procedure.

The chemical yield factor obtained from the analyzed standards was used in calculating the total zinc-69m activity from the activity obtained for the 5 eluates of each of the lung samples carried through the ion exchange procedure. The concentration of zinc was then determined using the mean of the two values of the standardization factor reported in Table 5. These standardization data are applicable only to samples irradiated at the same time as the standards.

d. Acetylacetone separation of manganese and copper. The ashed lung sample is dissolved in 2 ml of 5 M HCl. This solution is added to a 60 ml separatory funnel containing 15 ml of the acetate buffer solution and 1 ml of acetylacetone. The pH of the resulting solution is approximately 4.0. The funnel is shaken for exactly 1 minute in an automatic shaker. A 2 ml volume of chloroform is added and the funnel is again shaken for 1 minute. The chloroform layer is transferred to a counting tube and stoppered. Three additional extractions are conducted, with the same volumes of acetylacetone and chloroform added each time. The extracts are analyzed for manganese-56 and copper-64, using the 0.845 and 1.02 Mev peaks, respectively. The latter peak, resulting from the positron emission of copper-64 provides much greater sensitivity than does the 1.34 Mev peak.

The manganese and copper standards are aliquoted and analyzed in the manner described for the zinc standards in the preceding section, except that the acetylacetone separation procedure is applied to the split set of Cu and Mn standards after adding 1.0 ml of the Fe, Zn, and Cu carrier. All activities are measured by peak height. The manganese-56 values are calculated back to zero time, i.e. the time of removal of the samples from the Glory tube of the NRL reactor.

The precision for the manganese separations was not very satisfactory. The reasons for these variable manganese recoveries are being sought at present with additional experimentation. However, the chemical yield factors obtained for a given pair of standards have been used to calculate the total radioactivity of that nuclide in the lung samples irradiated at the same time.

e. Dithizone method for the separation of zinc. The aqueous portion remaining in the separatory funnel after the series of acetylacetone extractions is extracted twice with the 200 mg per liter solution of dithizone in CCl_4 to remove the zinc. Aliquoted zinc standards are carried through two dithizone extractions after first extracting with acetylacetone twice to simulate the treatment of the lung samples. The pH of the solution following the acetylacetone extraction is suitable for the extraction of zinc dithizonate as shown by a 92 to 96% recovery of zinc-69m from aliquoted standard samples.

The results of the zinc, copper, and manganese analyses completed to date are presented in Table 6. The number and the date of the irradiations and the radiochemical separation methods are included in this table to permit the comparison of results for a given element in separate aliquots of a lung sample irradiated on different dates and/or subjected to different separation procedures. Examination of these data

Table 6. Results of analysis of lung samples (µg/g dry lung).

Sample No.	Irradiation No. & Date	Radiochemical Separation Method	Zn	Mn	Cu
26943	1 (12-19-63)	Dithizone	28.0	--	--
	3 (3-5-64)	3 cm Ion Exchange[a]	23.1	--	9.6
26944	1 (12-19-63)	Dithizone	30.4	--	--
	3 (3-5-64)	3 cm Ion Exchange	42.4	--	11.2
	5 (4-7-64)	Acetylacetone	--	0.33	--
	7 (4-23-64)	Acetylacetone	--	0.70	4.0[b]
		Dithizone	38.2	--	--
26945	1 (12-19-63)	Dithizone	70.4	--	--
	2 (1-23-64)	3" Ion Exchange	--	--	9.6
	3 (3-5-64)	3 cm Ion Exchange	63.2	--	12.8
	5 (4-7-64)	Acetylacetone	--	0.16	--
	7 (4-23-64)	Acetylacetone	--	0.29	14.3[b]
		Dithizone	151.6	--	--
29647	2 (1-23-64)	3" Ion Exchange	--	--	6.7
	3 (3-5-64)	3 cm Ion Exchange	77.6	--	12.0
	7 (4-23-64)	Acetylacetone	--	0.54	9.7[b]
		Dithizone	54.0	--	--
26949	8 (5-5-64)	Acetylacetone	--	1.52	--
		Dithizone	32.0	--	--
26950	5 (4-7-64)	Acetylacetone	--	0.46	--
	7 (4-23-64)	Acetylacetone	--	0.21	7.1[b]
		Dithizone	59.8	--	--
26952	8 (5-5-64)	Acetylacetone	--	2.80	--
		Dithizone	51.0	--	--
26953	8 (5-5-64)	Acetylacetone	--	1.36	--
		Dithizone	41.4	--	--
26997	5 (4-7-64)	Acetylacetone	--	0.90	--
26998	5 (4-7-64)	Acetylacetone	--	0.12	--
27001	8 (5-5-64)	Acetylacetone	--	1.76	--
		Dithizone	39.4	--	--
27003	5 (4-7-64)	Acetylacetone	--	1.33	--

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[a] Ion Exchange: Dowex 1-X8, 20-50 mesh.
[b] Using annihilation radiation peak at 1.02 Mev.

will show that the precision of the methods (estimated to be equal or less than an error of 10% standard deviation) needs to be increased by improving the procedure for determining the chemical yields. It is believed that this may be done in the case of copper and zinc on the basis of experimentation in progress.

It is possible that the conditions of the acetylacetone method for the separation of manganese may be refined sufficiently to provide results with an acceptable degree of reproducibility. However, efforts in this direction must be discontinued at present to permit refinement of the procedures for copper and zinc.

A summarized tabulation of our analytical data is presented in Table 7 which contains, for comparative purposes, a summary of the values reported in the literature for the same elements in adult human lung samples from subjects who were victims of accidental death and ostensibly free of disease according to the reports of the examining pathologists. Examination of the data in Table 7 will show that our data are in the same concentration ranges as those of several investigators who used emission spectrographic procedures for the analysis of the trace element content of human lungs.

(R. G. Keenan and J. H. Marcus)

Table 7. Comparison of concentrations of zinc, copper, and manganese reported in normal human lung samples from adult victims of accidental death with those reported in Table 6 for current project (expressed as µg element per gram of dried tissue).

Investigators, and Year	Method of Ashing & Analysis	No. of Analyses	Zn		Cu		Mn	
			Range	Mean	Range	Mean	Range	Mean
Tipton & Cook, 1964	Dry Ashing; Spectrographic	141	29.4-151.9	68.6	2.5-12.3	6.4	0.25-8.3	1.2
Griffith, Butt, & Walker, 1954	Dry Ashing;	79	---	86.3			---	1.8
	Spectrographic	62			---	13.0		
Koch et al 1956	Wet Ashing;							
	Spectrographic;	4	40.8-124.1	98.0	---		---	---
	Colorimetric	5	---		4.4-11.3	7.4		
Current Project	Wet Ashing;	15	23.1-151.6	53.5	---	---	---	---
	Neutron Activation Analysis	10	---	---	4.0-14.3	9.7	---	---
		14	---	---	---	---	0.12-2.8	0.9

6. MISCELLANEOUS

This section of the progress report contains miscellaneous techniques of interest and usefulness to several areas but which do not particularly fit into any one category.

A. Positive Sealing with Optical Coupling of Radioactive Sources in Machined Plastic Phosphor Scintillators

If one is interested in doing high efficiency beta counting, a plastic scintillator is often the most convenient way. The usual method is to optically couple the scintillator to a phototube, and the light pulses are amplified and analyzed by a variety of electronic equipment. It is always necessary to incorporate a radioactive standard into the measurement technique. In order to assure that a standard can be safely handled over a long period of time, some type of positive sealing is necessary. The following paragraphs describe a technique which we find give a positive seal with retention of optical clarity at the seal.

Positive sealing of machined polyvinyltoluene plastic phosphor beta scintillators (NE-102, obtained from Nuclear Enterprises, Ltd., Winnipeg, Canada) was achieved using Carl Biggs No. 823 epoxy resin (Carl Biggs Company, Santa Monica, California). The procedure is as follows:

1) Thoroughly clean the plastic surfaces with methanol.

2) Cover exposed top of plastic sample container (see Figure 19) with Parafilm to prevent contamination with radioactive material. (Note 1).

3) Carefully pipet liquid radioactive solution into

plastic sample container.

4) Evaporate liquid material. (Note 2).

5) During the evaporation period (usually at least one hour) thoroughly mix nine drops of No. 823 resin and one drop of hardener. This quantity is sufficient for at least one scintillator.

6) Remove dissolved air from the mixed resin by applying vacuum. (Note 3).

7) After the radioactive solution has completely dried, remove the Parafilm from the sample container and cover both surfaces (top of container, bottom of lid) with the resin, using a spatula. (Note 4).

8) Carefully place the scintillator lid on the container, and place a 50-100 gram weight on the top of the scintillator. (Note 5).

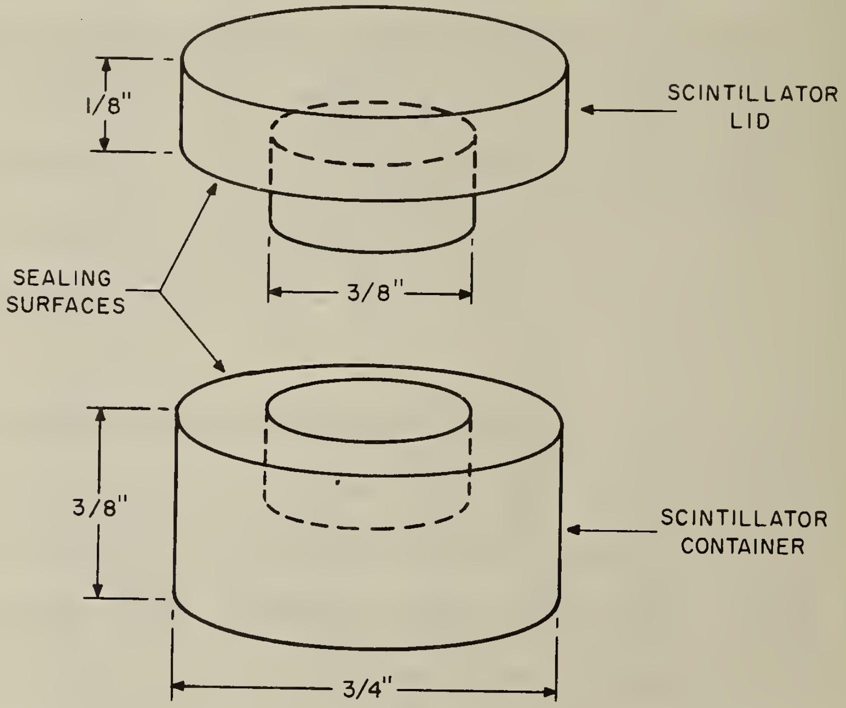

Figure 19. Beta scintillator, machined from NE-102 plastic phosphor.

Note 1. Before applying the Parafilm, a hole was punched in the film to allow depositing the radioactive material into the container. Care must be taken so the Parafilm does not come in contact with the white reflective coating around the outside of the scintillator, since the Parafilm has a tendency to remove the coating.

Note 2. Heat may be used to assist in evaporating the liquid sample, but caution must be used since the melting point of the plastic is around 75°C.

Note 3. A simple water aspirator applied through an inverted funnel with the resin in a small watch glass gave satisfactory results. A higher vacuum would be better.

Note 4. The resin should not be applied to a warm scintillator, since the decreased viscosity of the resin causes separation of the container and lid.

Note 5. If a piece of glass or clear plastic is used as the weight, the transparency of the seal may be continuously monitored. Small bubbles can be removed by lightly pressing on the weight.

Curing time of the resin is rather long, set at between 12 and 24 hours for complete hardening. The sealed scintillators may be gently handled after about two hours. This epoxy resin, when properly used, gives a highly transparent seal.

(D. A. Becker)

B. Ion Exchange Resins -- General Consideration

The most important consideration in any experiment is to control the variables so that reproducible results may be obtained. In Figure 20 and 21 are shown the apparatus for regeneration of ion exchange resins and for the gradient elution of an ion exchange column.

There is a need for regenerating new resins by taking it through several cycles in order to remove trace impurities. To obtain uniform resin size the resin ought to be back washed, (that is upward flow of water through an ion exchange resin to cleanse it of foreign material and reduce the compaction of the resin bed). Backwashing the resin is perhaps the most important step, and is the most often omitted step, in preparing a uniform clean resin.

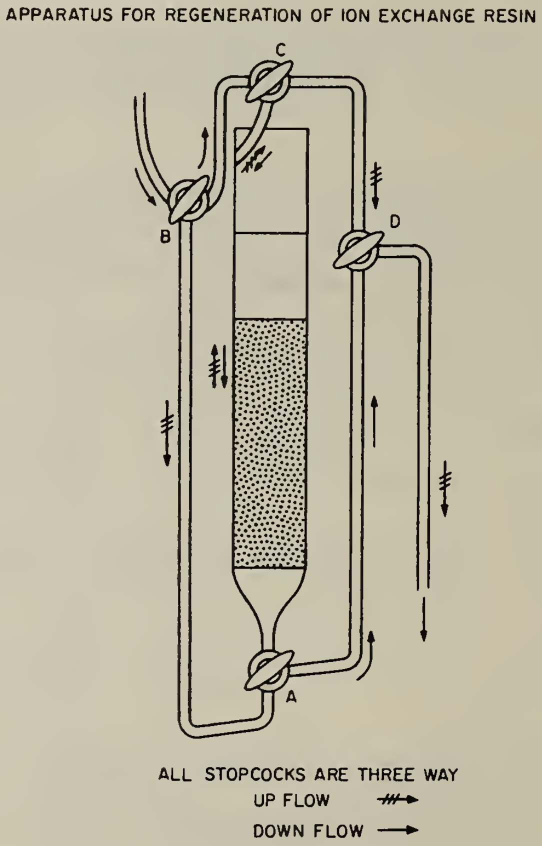

Figure 20. Apparatus for regeneration of ion exchange resin.

In Figure 20 is shown the apparatus for regeneration of an ion exchange resin. Three-way stopcocks were used.

When a cationic resin was used, the following procedure is employed:

1) The resin was washed upflow with thirty bed volumes of demineralized water. The stopcocks were opened so that the water flows through B to A to C and out through D.

2) The resin was changed downflow with 6 N HCl to remove any iron present. The valves were opened so that the acid flows from B to C through the column to A and out through D. It is to be noted that the stopcock D is located above the resin level so that the resin can never go dry.

3) The acid wash was followed by thirty bed volumes of demineralized water.

4) The resin was converted to the sodium form with 5% sodium hydroxide. The resin is converted to the sodium form by running the base through the column upflow to allow for expansion.

5) The resin was then treated with sixty bed volumes of a 1% solution of EDTA. The EDTA was passed through the column downflow as was another thirty bed volumes of demineralized water.

6) The resin was then washed with demineralized water flowing upward through the resin.

Figure 21 shows an apparatus for gradient elution studies of an ion exchange resins. The charging solution enters the columns through stopcock No. 8. The column could be eluted with varying solutions through stopcocks 4,5,6,7 and enter the columns through 9 and 10 respectively. After the experiment is complete the column is regenerated and washed with non-ionic detergent pumped from 2 through the apparatus. The column would be washed upflow by opening stopcock No. 3, No. 9 to No. 11 to No. 13 and No. 10 to 12 to No. 14. This would be followed by demineralized water.

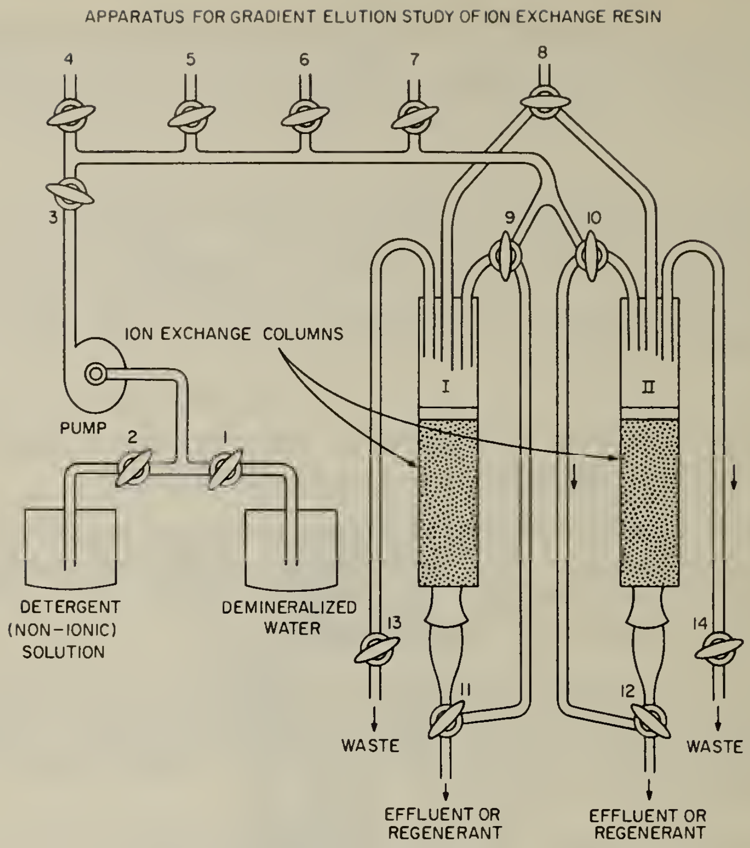

Figure 21. Apparatus for gradient elution study of ion exchange resin.

(A. R. Langrebe)

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