Conf-821046--2

CONCURRENT REDUCTION AND DISTILLATION: AN IMPROVED TECHNIQUE FOR THE RECOVERY AND CHEMICAL REFINEMENT OF THE ISOTOPES OF CADMIUM AND ZINC*

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CONF-821046--2

DE83 001931

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For presentation at the 11th World Conference of the International Nuclear Target Development Society, October 6-8, 1982, Seattle, Washington.

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*Research sponsored by the Office of Basic Energy Science, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

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CONCURRENT REDUCTION AND DISTILLATION - AN IMPROVED TECHNIQUE FOR THE RECOVERY AND CHEMICAL REFINEMENT OF THE ISOTOPES OF CADMIUM AND ZINC

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ABSTRACT

The Electromagnetic Isotope Separations Program of the Oak Ridge National Laboratory has been involved in the separation, chemical recovery, and refinement of the stable isotopes of cadmium and zinc since 1946. Traditionally, the chemical refinement procedures for these elements consisted of ion exchange separations using anion exchange resins followed by pH-controlled hydrogen sulfide precipitations. The procedures were quite time-consuming and made it difficult to remove trace quantities of sulfur which interferes in subsequent attempts to prepare rolled metal foils. As demands for ^{113}Cd and ^{68}Zn (a precursor for the production of the radiopharmaceutical ^{67}Ga) increased, it became evident that a quicker, more efficient refinement procedure was needed. Details of an improved method, which employs concurrent hydrogen reduction and distillation in the recovery and refinement of isotopically enriched zinc, are described. Modifications of the procedure suitable for the refinement of cadmium isotopes are also described.

1. INTRODUCTION

The Electromagnetic Isotope Separations Program of the Oak Ridge National Laboratory has been involved in the separation, chemical recovery, and refinement of the stable isotopes of zinc and cadmium since 1946. The initial interest was in obtaining small quantities of isotopically enriched samples of each of the stable isotopes of these elements for use in basic physical research. Recently, the emphasis has shifted to reflect demand by the medical community for the radiopharmaceutical ^{67}Ga which is produced by a (p,2n) reaction on ^{68}Zn. Following the discovery by Hayes and Edwards[1] at the Oak Ridge Associated Universities Medical Division in 1969 that ^{67}Ga localizes in soft malignant tumors (lymphomas and lymphatic-associated diseases) and is easily measured by external scintillation cameras, there was a dramatic increase in the demand for ^{68}Zn. In the ten year period from 1970 to 1980, the ORNL annual distribution of ^{68}Zn increased by approximately 3,000%. During the mid nineteen sixties there was a similar increase in demand for ^{113}Cd, which is used primarily for thermal neutron filters but, in recent years, that demand has decreased. There is, however, a continuing interest in other stable isotopes of cadmium, particularly ^{114}Cd and ^{112}Cd which are used in the fabrication of lasers and as a precursor to the radiopharmaceutical ^{111}In, respectively.

2. PROCEDURES

2.1 Traditional Procedure for Zinc

As is true for most procedures for recovery and refinement of stable isotopes, our procedure for zinc has been a modified "classical" gravimetric analytical procedure. In discussing the analytical chemistry of zinc, James H. Kanzelmeyer[2], says "Although zinc has been important in commerce since the beginning of the history of metallurgy, its analytical chemistry is not as clear-cut nor as adequately developed as that of most commercial metals. The "classical" analytical chemistry of zinc is characterized by a wealth of proposed methods, but a paucity of solidly established procedures; an abundance of empirical and semiquantitative estimations developed for particular applications, but a lack of generally useful determinations based upon theoretical and stoichiometric relationships".

Briefly, our traditional procedure for recovery the and refinement of stable isotopes of zinc was as follows: The isotopes were received in the chemistry laboratory in water-cooled, copper calutron receiver pockets with relatively small quantities of zinc alloyed with large amounts of copper (Fig. 1). The zinc-copper alloy was leached from the pockets with nitric acid and the nitrates converted to chlorides by repeated evaporations and additions of hydrochloric acid. The chloride solution was adjusted to approximately 2 N hydrochloric acid, loaded on Dowex-1 anion exchange resin column, and the column washed with 2 N hydrochloric acid to elute the copper from the column while leaving the zinc adsorbed on the resin. The zinc was eluted from the column with distilled water followed by 3 N ammonium hydroxide. The eluted zinc solution was adjusted to approximately 1 N hydrochloric acid, saturated with hydrogen sulfide and filtered to remove the acid sulfide group of contaminants. The solution was diluted to double its volume with distilled water, adjusted to pH 3 with ammonium hydroxide, buffered with citric acid, and again saturated with hydrogen sulfide. The precipitated zinc sulfide was filtered on a fritted glass funnel, washed, dried, and ignited to zinc oxide at 1000°C. The zinc oxide was dissolved in acetic acid, zinc oxalate precipitated by addition of oxalic acid, filtered, dried, and ignited back to zinc oxide at 1000°C. If zinc metal were desired, it was produced by electrodeposition on a tantalum cathode from a zinc chloride-ammonium chloride solution.

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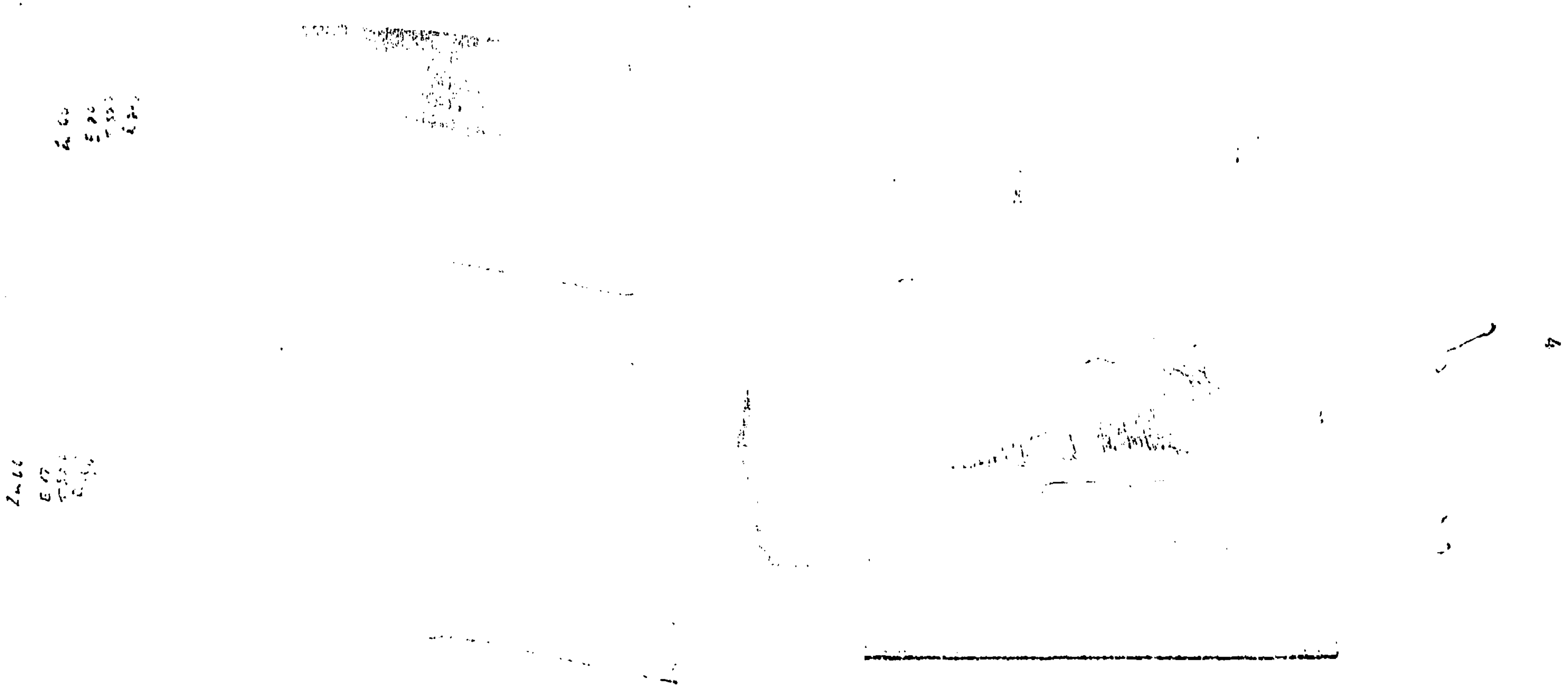

Fig. 1. Calutron receiver pockets for isotopically enriched ^{66}Zn.

2.2 Rationale for A Different Procedure

This traditional refinement procedure gave generally satisfactory results but it was quite time-consuming, not very well adapted to large size samples, and frequently resulted in traces of sulfur in the final product. This was cause for concern since trace quantities of sulfur make it difficult to produce zinc metal which can be rolled into a foil. As the demand for ^{68}Zn increased, this concern became more urgent and it was evident that a refinement procedure was needed in which the use of sulfur compounds was minimized or eliminated. Obviously, a distillation procedure would meet this requirement if it proved practical in other respects.

2.3 Distillation as a Refinement Technique

The use of vacuum distillation as a technique in the refinement of isotopically enriched samples is well known. In a paper presented at the 1978 Annual Meeting of this Society, Kobisk and Adair[3], of the Oak Ridge National Laboratory Isotope Research Materials Laboratory, described a procedure for pyrochemical reduction with a reducing metal and subsequent removal of the isotopic product metal by vacuum distillation. This procedure is especially useful in reduction of the alkaline earth and rare earth groups of elements. In the Isotope Separations Section of ORNL, various distillation techniques have been used in the recovery and refinement of isotopes of chlorine, bromine, sulfur, mercury, osmium, ruthenium, argon, and xenon.[4–6] Procedures for separation of zinc and cadmium from other elements by vacuum distillation have also been described. In 1949, Balis, Brink and Liebhafsky[7] described a procedure in which metallic zinc was distilled from a copper boat in a determination of the percentage of zinc oxide in metallic zinc, and in 1972, Kellner[8] described a procedure for distilling a small amount of isotopic cadmium for mass spectrometric isotopic analysis.

2.4 Experimental Distillation of Zinc

As a general rule, different compounds or elements can be separated by distillation if their pressures at a controllable temperature differ by at least two orders of magnitude.[3] The vapor pressure of zinc at 1100°K (827°C, approximately 250°C below the melting point of copper) is reported by Nesmeyenov[9] as 3.08×10^{2} mm Hg while for copper it is only 3.92×10^{-7} mm Hg. Thus it appears that the vapor pressure of zinc is sufficient to make its distillation at atmospheric pressure practical at a reasonably attainable temperature. To test the distillation separation of zinc from copper under conditions similar to those encountered in the refinement of separated isotopes, two grams of zinc oxide and twenty grams of copper oxide were mixed, transferred to a Vycor boat and loaded into a quartz combustion tube in a tube furnace (Fig. 2). Two gas scrubbers were used to wash the exhaust gases, the first containing approximately 5 N nitric acid and the second, distilled water. Then the gases were vented to a fume hood. A flow of argon was started and the temperature of the tube furnace raised to 850°C. As the argon flow was reduced and purified hydrogen substituted for it, there was evidence of reduction of both oxides and slow volatilization of zinc. The furnace temperature was raised to 1000°C and held at this point for three hours with hydrogen

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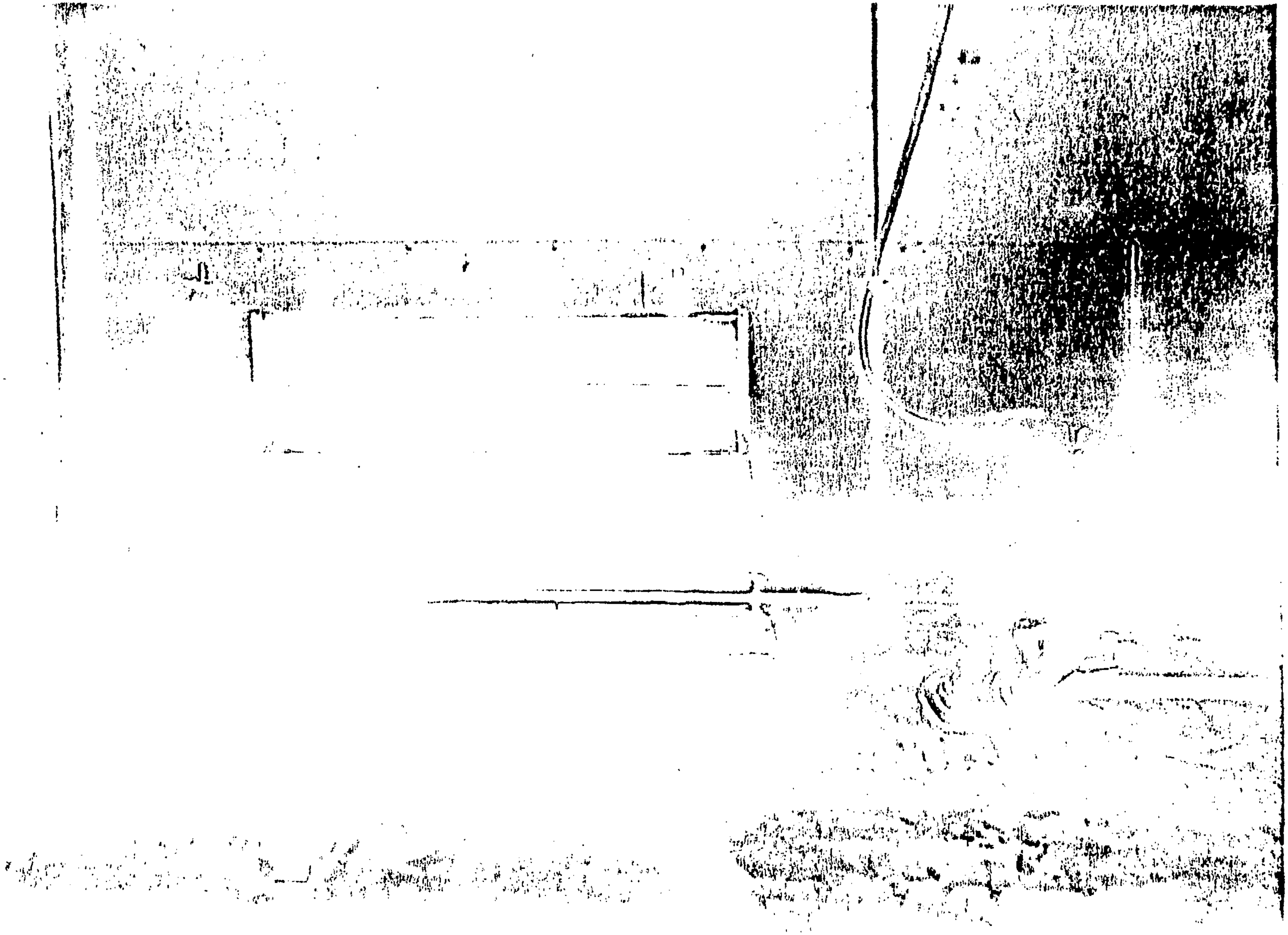

Fig. 2. Apparatus for distillation of isotopically enriched zinc.

flow. Then the gas was switched back to argon and the same temperature maintained for an additional five hours. The furnace was turned off and, after cooling, the boat removed from the combustion tube. Visual inspection indicated that the zinc had been distilled and condensed on the cool end of the tube, leaving a porous mass of copper metal in the boat. The zinc was dissolved from the combustion tube with approximately 8 N nitric acid and the tube rinsed with distilled water. These wash solutions were combined with the gas scrubber trap solutions, filtered, and evaporated to near dryness. Oxalic acid was added to the solution, the resultant zinc oxalate taken to dryness under a heat lamp, then ignited to zinc oxide. Weighing the zinc oxide confirmed that 96.4% of the available zinc had been recovered by this first distillation. The copper residue was chemically reprocessed to copper oxide and a second distillation yielded an additional 2% of the zinc, giving a total recovery of greater than 98%. Preliminary spectrographic analysis of the zinc oxide showed trace amounts of copper and lead as contaminants. Several additional samples gave similar results in recovery and chemical purity.

2.5 Distillation Recovery and Refinement of Isotopic Zinc

The following procedure was adopted and is now used routinely in the recovery and refinement of isotopes of zinc. The water line is removed from the calutron receiver pocket, the outside of the pocket cleaned with nitric acid and water, then dried and covered with electroplating tape. The purpose of this step of the procedure is to minimize chemical contamination from the solder used to attach the water line and, more importantly, to avoid isotopic contamination from normal zinc which might have condensed on the outside of the pocket. Tape is removed from the front of the pocket, the major portion of the zinc-copper alloy is physically removed, and the pocket leached with approximately 8 N nitric acid to remove the last traces of zinc. When all the alloyed zinc has been removed from the pocket and dissolved in hot nitric acid, the solution is diluted to approximately 4 N nitric acid and filtered. It is evaporated to near dryness, transferred to a Vycor or quartz evaporating dish, oxalic acid added, the resultant zinc and copper oxalates taken to dryness under a heat lamp and then ignited to their respective oxides at 1000°C in a muffle furnace. (Copper nitrate and zinc nitrate solutions can be taken to dryness and ignited directly to their oxides, but this results in considerable spattering and the physical form is predominantly hard lumps rather than the fine powder obtained from ignition of the oxalates.) The mixed oxides are hydrogen-reduced and the zinc distilled and dissolved from the tube with nitric acid as previously described. The zinc nitrate solution is adjusted to approximately 3 N nitric acid, filtered, and electrolyzed at two volts for one hour using platinum gauze anode and cathode. Traces of lead and copper that have been carried along with the distilling zinc are deposited on the anode as lead peroxide and on the cathode as elemental copper. The solution is evaporated, converted to zinc oxalate, then to zinc oxide as before.

2.6 Distillation Recovery and Refinement of Isotopic Cadmium

The recovery and refinement procedure we originally used for cadmium isotopes was very similar to that for zinc, consisting primarily of anion exchange and hydrogen sulfide precipitations. This procedure suffered from the same basic disadvantages mentioned previously in that it was slow and made it very difficult to eliminate residual sulfur in the product isotopes. A hydrogen reduction-distillation procedure very similar to the one used for zinc has been adopted for cadmium. Cadmium isotopes are collected in water-cooled aluminum receiver pockets so the chemistry required for conversion to the oxides prior to distillation is somewhat different from that described for zinc. The receiver pockets are cleaned, the major portion of the aluminum-cadmium alloy physically removed from the pocket and the remainder leached with nitric and hydrochloric acids. When all solids are dissolved, the solution is evaporated to beginning crystallization, then diluted with distilled water and filtered. The cadmium is precipitated from solution by the addition of 6 N sodium hydroxide. Additional 6 N sodium hydroxide is added until the major portion of the amphoteric aluminum hydroxide has gone back into solution. The cadmium hydroxide, along with some entrained aluminum hydroxide, is separated by centrifuge, dissolved in a minimum amount of hydrochloric acid, diluted, and cadmium carbonate precipitated by the addition of ammonium carbonate. The cadmium carbonate is filtered on a medium fritted glass filter, washed with distilled water to remove ammonium chloride, dried, and ignited to cadmium oxide at 500°C. The reduction-distillation of isotopic cadmium is similar to that described for zinc with the exceptions that a boat of purified graphite is used rather than quartz and the reduction-distillation is accomplished at a temperature of 800°C. After distillation is complete, the cadmium metal is dissolved from the combustion tube with nitric acid, the solution evaporated to near dryness to expel excess nitric acid, and diluted with distilled water. Another carbonate precipitation is made and the cadmium carbonate again ignited to cadmium oxide at 500°C. If cadmium metal is desired, it may be produced by the same electrolytic procedure used for zinc or it may be obtained by hydrogen reduction in graphite at 400°C. For years we, and our customers, were concerned with atmospheric oxidation of finely divided metal samples of isotopic cadmium until we found that samples originating from a chloride solution are much less subject to this problem than are those originating from a nitrate solution.[10] For this reason, when several preliminary samples of individual receiver pockets, which have similar isotopic enrichment, are to be combined into a final sample, the cadmium oxide is dissolved in hydrochloric acid and the carbonate precipitation made from a chloride solution. Figure 3 shows isotopic cadmium metal which has been hydrogen reduced and sealed in evacuated ampules. Such ^{112}Cd and ^{114}Cd samples are available from ORNL Isotope Sales Office.

3. CONCLUSIONS

Four samples were submitted to the Analytical Chemistry Division for spark source mass spectrometry analyses. Two were old samples of isotopically enriched ^{67}ZnO and ^{110}CdO which had been purified by traditional gravimetric procedures, and two were more recent samples of

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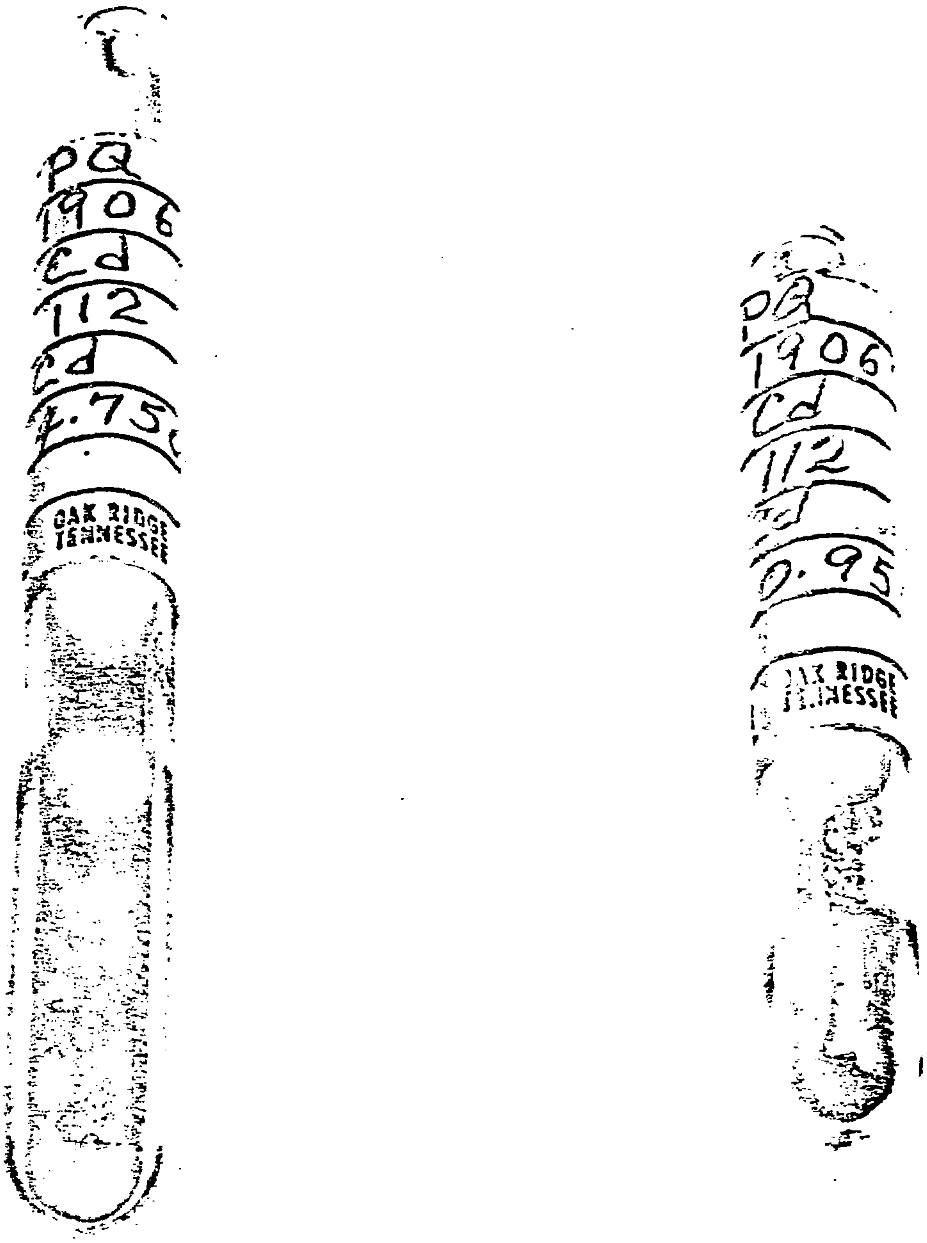

CADMIUM METAL

97.05% ^{112}Cd

isotopically enriched ^{67}ZnO and ^{110}CdO which had been purified by the concurrent reduction and distillation procedures described above. Table 1 lists the results of these analyses but includes only those elements for which contamination levels of greater than one part per million were found. In spark source mass spectrometric analysis, an indeterminate number of ions become doubly charged and appear at one half their normal mass positions. Thus ^{68}Zn will appear to be ^{34}S, ^{66}Zn will appear to be ^{33}S, and ^{64}Zn will appear to be ^{32}S giving a total of 95.27% of all doubly charged ions of normal zinc interfering with sulfur analyses. Since isotopically enriched ^{67}Zn will not mask sulfur analyses, it was chosen for the comparison of purification methods. Note that in the two samples of ^{67}ZnO, the total detected contamination has been reduced from 1300 ppm to 320 ppm or, conversely, the chemical purity has been increased from 99.87% to 99.97% by the new procedure. The comparison of results for cadmium are less conclusive due to the masking influence of cadmium preventing an analysis for iron and normal zinc contamination preventing an accurate analysis for sulfur. However, other total detected contamination has been reduced slightly and experience with preparing malleable cadmium metal indicates considerable improvement in quality from a more rapid and greatly simplified procedure.

Although unproved at the present time, we feel that this procedure may also be useful in the recovery of targets of isotopic zinc or cadmium from backings of aluminum, nickel, or graphite.

Table 1.

Comparison of methods of purification of zinc and cadmium (ppm contamination).

Contaminant	Gravimetrically purified ^{67}ZnO	Distillation purified ^{67}ZnO	Gravimetrically purified ^{110}CdO	Distillation purified ^{110}Cd
Al	20	3	30	6
B	20	20	30	5
Ba	10	30	20	3
Ca	10	3	30	10
Cd	8	10	major	major
Cr	3	20	8	10
Cu	100	1	1	30
Fe	40	20	masked	masked
K	200	20	100	30
Mg	3	1	6	2
Na	400	100	50	60
Ni	5	1	1	1
Pb	50	5	7	40
S	200	60	masked	masked
Si	30	20	300	7
Zn	major	major	50	200
TOTAL	1300	320	630	400
(Two significant figures)				

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