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Supplement I
UC-22 - Isotope Separation

PREPARATION OF CHARGE MATERIALS FOR ORNL
ELECTROMAGNETIC ISOTOPE SEPARATORS

Supplement I

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PREPARATION OF CHARGE MATERIALS FOR ORNL
ELECTROMAGNETIC ISOTOPE SEPARATORS

SUPPLEMENT I

C. W. Sheridan, H. R. Gwinn, and L. O. Love

ABSTRACT

Since publication of the previous charge preparation report,¹ a number of other chemical compounds have been evaluated. The preparation of those charge materials which result in either greater ion output, better isotopic purity, higher ion retention, or smoother operation in the separator is discussed in this supplement.

INTRODUCTION

During the interval since the charge preparation report appeared, a number of chemical compounds have been prepared and evaluated as potential charge materials in the ORNL electromagnetic separators. Some of these materials have proved to be superior to compounds previously considered as "preferred" since they have resulted in greater ion output reaching the collector pockets and better isotopic purity; have provided higher ion retention; or, in some cases, have permitted smoother operation in the separator.

This supplement describes the preparation of tin(II) sulfide, rubidium carbonate, silicon(IV) sulfide, ruthenium(V) fluoride, iridium(VI) fluoride, and disulfur dichloride and the subsequent use of these compounds in separation of the isotopes of tin, rubidium, silicon, ruthenium, iridium, and sulfur, respectively. Improvements are noted in each case, usually by means of a comparison with previous isotope separations.

¹C. W. Sheridan, H. R. Gwinn, and L. O. Love, Preparation of Charge Materials for ORNL Electromagnetic Isotope Separators, USAEC Rpt. ORNL-3301, Oak Ridge National Laboratory (July 1962).

REVISED CHARGE COMPOUND FOR IRIDIUM²

Charge transport stability systems developed recently have enabled the controlled vaporization of ruthenium and iridium fluorides, compounds previously considered too unstable for use as charge materials. Previously, the separation technology for platinum metals was severely limited since only the nonvolatile platinum metals themselves could be used as charge material. These metals were vaporized by 35-keV electron bombardment heating and only an unsteady flow of platinum metal vapor to the arc region could be maintained. Separation runs lasted only a few hours, ion outputs were erratic with a very low average, and the instability of the separation limited the isotopic purity. The electromagnetic separation process could not be optimized under these conditions.

The first successful separation of iridium isotopes using IrF_6 as charge material was carried out in November 1964. The superior run stability and duration, higher ion output reaching the collector, and improved process efficiency achieved in this series are compared in Table 1 with results from the best prior series. Some variation in performance is encountered but two runs have reached the performance level shown in Table 1.

Table 1. Comparison of Electron Bombardment Heating
With Capillary Transport for Iridium Separations

Charge transport system	Charge material	Run duration, hr	Total ion output, ma		Process efficiency, %
			Average	Peak	
Capillary	IrF_6	20-30	3.0	10.8	3.1
Electron bombardment	Ir	2-9	0.5	7.8	0.9

Iridium hexafluoride was prepared as the feed material for the calutrons for use in the separation of iridium isotopes. The preparation was conducted with batches of ~150 g of finely powdered iridium metal in a nickel reactor at 300°C, using undiluted elemental fluorine. A vacuum manifold system of nickel was used during the fluorination.

²Ibid, p. 34.

The iridium metal was placed in the reactor, and the system was evacuated and leak tested at room temperature. Fluorine was cautiously admitted to the reactor to desensitize any reactive materials, and volatile reaction products were removed by vacuum distillation. The temperature of the reactor was then raised to 300°C and the fluorine pressure was maintained between 10 and 30 psi. The iridium hexafluoride produced was vacuum distilled periodically from the reactor into a calutron charge bottle which was cooled in a dry-ice slush bath. For each batch, ~200 g of iridium hexafluoride was removed from the reactor and system and transferred into calutron bottles. Iridium hexafluoride is pale yellow and highly volatile, has a density of 6.0 and a boiling point of 53°C, and is violently reduced by water. In order to minimize decomposition, the material must be handled in charge bottles and transport systems constructed of nickel and pretreated with fluorine.

REVISED CHARGE COMPOUND FOR RUBIDIUM³

Rubidium chloride was the preferred charge compound in four previous electromagnetic separations of rubidium isotopes. Rubidium iodide was also tried but failed to perform as well as the chloride. Both compounds, however, caused heavy sparking in the ionization area and required constant attention to maintain focus. Rubidium carbonate, Rb_2CO_3 , was used during 13 of the 44 innage runs comprising the most recent separation (Series LY) and was found to (1) reduce sparking to a minimum thereby leading to smoother operation, (2) use less charge material per innage hour (lower CCR), (3) increase the total ion output (higher collection rate), and (4) utilize the charge input more efficiently (higher process efficiency). A comparison of calutron parameters obtained by using RbCl and Rb_2CO_3 in the recent separation is shown in Table 2.

Table 2. Comparison of Charge Materials in Series LY

Charge material	Charge consumption rate, g Rb/innage hr	Average run duration, hr	Total ion output, ma		Process efficiency, %
			Average	Peak	
RbCl^*	0.52	58.5	9.9	15.2	6.5
$\text{Rb}_2\text{CO}_3^{**}$	0.36	83.1	15.7	22.2	17.3

*20 calutron runs.

**13 calutron runs.

Charge variations, such as the passage of carbon tetrachloride over the carbonate and addition of catalytic agents (MnO_2 , CeO_2 , platinum metals, and TlCl) to promote the reaction of CCl_4 with Rb_2CO_3 , were tried but none were found superior to carbonate alone.

It is not known with certainty what volatile form of rubidium is obtained following decomposition of the carbonate in the ion source, but there are strong indications that it is the metal. Although it is known⁴ that Rb_2CO_3 decomposes to Rb_2O if heated at elevated temperatures, little is reported

³Ibid, p. 59.

⁴H. Remy, Treatise on Inorganic Chemistry, Vol. I, Elsevier Publishing Co., Amsterdam, 1956, p. 193.

concerning the vapor characteristics of the oxide. Brewer and Mastick,⁵ in a paper published in 1951, state as a result of theoretical calculations that all of the gaseous alkali oxides except Li_2O are unstable with respect to dissociation and, therefore, tend to vaporize in the elemental states. Brewer and Margrave⁶ in 1955 and then Berkowitz et al.⁷ in 1959 ascertained that $\text{Li}_2\text{O}(\text{s})$ gives a gaseous oxide above 1000°C but reiterate that the most probable gaseous species over rubidium and cesium oxides are the elements.

Rubidium carbonate can be purchased from commercial suppliers; however, it can also be prepared very simply in the laboratory from other rubidium salts by means of a cation exchange technique. Rubidium chloride, for example, is passed through Dowex-50 ion-exchange resin in the hydrogen form, which adsorbs the rubidium and permits hydrochloric acid to pass through. Rubidium is then eluted quantitatively with ammonium carbonate solution.

⁵L. Brewer and D. F. Mastick, Theoretical Calculation of the Stability of Solid and Gaseous Alkali and Alkaline Earth Oxides, J. Am. Chem. Soc. 73: 2045 (1951).

⁶L. Brewer and J. Margrave, The Vapor Pressures of Lithium and Sodium Oxides, J. Phys. Chem. 59: 421 (1955).

⁷J. Berkowitz et al., Mass Spectrometric Study of the Sublimation of Lithium Oxide, J. Phys. Chem. 63: 644 (1959).

REVISED CHARGE COMPOUND FOR RUTHENIUM⁸

Until recently, development of separations technology for the platinum metals has been severely limited since only the platinum metals themselves could be used as charge material. These metals could be vaporized only by using 35-keV electron bombardment heating units, which provided a fluctuating flow of metal vapor to the arc region. Separation runs lasted only a few hours, ion outputs were erratic with very low averages, and the instability of the separation limited the isotopic purities which could be achieved.

Charge transport systems have now been developed which allow controlled vaporization of ruthenium and iridium fluorides, compounds previously considered too unstable for use as calutron charge materials. The first successful separation of ruthenium isotopes using the capillary transport concept with RuF_5 was carried out in May 1964. As shown in the following comparative data (Table 3), all operational parameters for these runs were improved over the best results achieved in previous separation runs.

Table 3. Comparative Data on Ruthenium Separations

Charge transport system	Charge material	Run duration, hr	Ion output, ma		Process efficiency, %	⁸⁸ Ru isotopic purity, %
			Average	Peak		
Electron bombardment	Ru	3-12	2.47	19.8	1.6	91.1
Capillary	RuF_5	30-40	14.8	29.7	3.5	98.9

Ruthenium pentafluoride, used as feed material for the calutron separation of ruthenium isotopes, was synthesized by reacting elemental fluorine with powdered metallic ruthenium in a nickel reactor. The fluorination system, consisting of a vacuum-pressure manifold and reactor (2-1/4 in. dia by 16 in. length), was constructed entirely of nickel and treated with gaseous fluorine at 300°C to prevent corrosion and decomposition of the pentafluoride. Approximately 200 g of powdered ruthenium metal was placed in the reactor, and the system was evacuated and leak tested. Fluorine was cautiously added to the system at room temperature to react with any

⁸ORNL-3301, op. cit., pp. 60-1.

impurities (e.g., silicon, carbon, iron, water vapor) that might be present in the metal, and these volatile products were removed by vacuum distillation. The temperature of the reactor was increased to 300°C, and the pressure of the fluorine was maintained between 10 and 30 psi. The pentafluoride was periodically vacuum distilled from the reactor and collected in a calutron charge bottle, which was cooled in ice water.

Ruthenium pentafluoride has a melting point of 106°C, boils at 313°C, and is a very corrosive material. It reacts violently with water decomposing into the tetroxide and other lower oxides. In order to minimize decomposition, the material must be handled in charge bottles and transport systems constructed of nickel and pretreated with fluorine.

REVISED CHARGE COMPOUND FOR SILICON⁹

A request for 100-g quantities of ²⁹Si and ³⁰Si at >95% isotopic purity motivated a special investigation for methods of increasing both ion output and isotopic purity. (The highest isotopic purity previously achieved for these isotopes was 91.85% ²⁹Si and 91.6% ³⁰Si.) Attempts to increase the ion output by using SiCl₄ as a charge material were not successful, and a survey was made of other silicon compounds in order to select a more suitable material.

As shown in Table 4, the results obtained using SiS₂ demonstrated that one of the objectives (higher ion output) could be accomplished using a charge material having a lower vapor pressure.

Table 4. Outputs Achieved With Silicon Charge Materials

Charge material	Ion output, ma*	
	Average	Peak
SiCl ₄	18.9	35.3
Si + I ₂	4.4	--
SiS ₂	47.2	80.3
SiS ₂ + Si	59.6	175.7

*Measured at the receiver.

Subsequent mass analyses of samples collected in the experimental program showed that >95% isotopic purity was also being obtained.

Experimental amounts of SiS₂ were prepared in the charge preparation laboratory by the reaction

The Al₂S₃ was synthesized by reacting one part aluminum powder with two parts of sulfur in a clay crucible. The Thermit-type reaction was triggered by inserting magnesium ribbon into the thoroughly mixed mass and igniting the ribbon. At the time the ribbon was lit, a safety can was placed over the crucible to control spattering. The crucible and safety can were contained in a metal tray, and all work was carried out in a fume hood. The

⁹Ibid, p. 65.

reaction was spontaneous, self-propagating, and very exothermic. The resulting Al_2S_3 was finely ground in a dry box under inert atmosphere, and the excess sulfur was removed by heating the mixture in a two-part glass reactor under vacuum at 400°C .

A quantity of Al_2S_3 , 10% in excess of stoichiometric, was ground with SiO_2 . The mixture was placed in a two-part quartz reactor and heated to 1100°C . At this temperature, SiS_2 formed, vaporized, and then condensed in the cool portion of the reactor. The product was removed from the reactor (in an inert atmosphere), transferred to a graphite charge bottle, and stored in this container under anhydrous conditions until used.

The large quantities of SiS_2 used during the extended separation series were procured from commercial sources. The commercially prepared material contained ~10% free sulfur and this was removed by heating the material in an evacuated system at 400°C before it was used in the calutron. The final charge material consisted of two parts SiS_2 and one part elemental silicon.

The use of SiS_2 not only increased ion outputs and provided higher purities for silicon isotopes but it also permitted the simultaneous collection of the isotopes of sulfur. Table 5 shows comparative data on the silicon separations.

Table 5. Comparative Data on Silicon Separations

Charge material	Product monitored per innage hr, mg	Innage, %	Charge consumption rate, g/hr	Isotopic purity, %	
				^{29}Si	^{30}Si
SiCl_4	19.9	87.7	0.29	91.85	91.6
$\text{SiS}_2 + \text{Si}$	62.6	78.0	0.88	95.28	95.55

REVISED CHARGE COMPOUND FOR SULFUR¹⁰

A number of sulfur compounds have been evaluated experimentally in efforts to find a charge system which would aid in obtaining higher purity ³³S. Sulfur-33, essentially free of ³²S, is a target material in the production of ³³P, which is a valuable nuclide in the study of certain biological systems.

Of the compounds tested, disulfur dichloride (S₂Cl₂) gave the highest ³³S isotopic purity; in addition, the use of this compound permitted the simultaneous collection of chlorine isotopes as valuable by-products. Table 6 shows the results obtained in recent isotope separations using S₂Cl₂ and CS₂ as charge material.

Table 6. Separation Results Using Carbon Disulfide and Disulfur Dichloride

Charge material	Innage, %	Ion output, ma		Charge consumption rate, g/hr	Process efficiency, %	³³ S purity, %
		Average	Peak			
CS ₂	83.5	31.3	61.5	1.6	2.3	25.1
S ₂ Cl ₂	59.6	39.8	59.3	0.7	7.2	61.15

Disulfur dichloride is usually prepared by the direct union of the elements. Elemental sulfur is melted in a flask and distributed uniformly on the inside surface by rotating the flask as the sulfur cools. Air is excluded, and dried chlorine is introduced into the flask. The reaction, $2S + Cl_2 \rightarrow S_2Cl_2$, proceeds quite smoothly when the flask is heated to 60-80°C using a flame. The reaction product is an orange-red liquid which has a repulsive, suffocating smell and fumes in moist air. It is readily hydrolyzed to give SO₂, S, and HCl. As prepared, the liquid is usually impure mainly due to dissolved starting materials although SCl₂, which decomposes at 59°C, may be formed by the action of excess chlorine with S₂Cl₂.

Since chlorine is extremely corrosive, especially to sensitive valve parts, S₂Cl₂ is purified by distillation prior to use in the separator. The liquid is transferred to an all-glass distillation system, excess

¹⁰Ibid, p. 68.

sulfur is added, and the fraction which distills between 137 and 142°C at atmospheric pressure is retained. The purified S_2Cl_2 is transferred to tared 500-ml round-bottom Pyrex flasks and reweighed to determine the sulfur content. The flasks are fitted with rubber stoppers bored to accept 2- to 3-in. lengths of stainless steel tubing (1/4 in. o.d.) which are used to connect ~18-in. lengths of gum rubber tubing (1/4 in. i.d.). The flasks are mounted outside the separator and the rubber tubing is fastened to a valve arrangement similar to that described for CCl_4 internal chlorinations.¹¹ Usually it is necessary to heat the flasks (e.g., with heat lamps) to obtain sufficient vapors in the ion source.

¹¹Ibid, pp. 5-7.

REVISED CHARGE COMPOUND FOR TIN¹²

Recent evidence indicates that free chlorine, released in the decomposition and ionization of SnCl_4 , reduces retention of tin isotopes at the collector pockets by chlorinating the separated isotopes and forming volatile compounds which migrate from the pockets. In an effort to reduce this loss, especially for isotopes of low natural abundance, SnS was used almost exclusively during the recently completed tin separation series. This compound was selected because (1) it was considered to be stable and volatile (2) its vapor pressure characteristics appeared suitable for use in conventional ion sources, and (3) sulfur was considered to be less reactive with the collected isotopes than chlorine.

Early runs with SnS showed extremely high charge-consumption rates, which indicated that some charge decomposition was occurring. To reduce this decomposition, hydrogen sulfide was passed over the heated material in the charge bottle and allowed to enter the ionization area mixed with volatilized SnS . This stabilizing effect resulted in a lower charge-consumption rate and also produced higher ion outputs.

Initial amounts of SnS were prepared by dissolving mossy tin metal in concentrated HCl , diluting with water, and precipitating with hydrogen sulfide to form the black sulfide, SnS . [It was found later that hydrogen sulfide can be introduced into the solution more readily through the addition of $(\text{NH}_4)_2\text{S}_x$ with compensating additions of HCl to maintain acidity.] Treatment was continued until all tin was precipitated, and the mixture was digested at low heat to allow the precipitate to coagulate and settle.

The precipitate was decant-washed three times in the beaker with water, to remove the bulk of ammonium chloride, and then transferred to a 2400-ml sintered-glass funnel where it was vacuum filtered and allowed to air dry. The solid was transferred to a large Pyrex boat which was placed in a 4-in. Pyrex tube and heated under vacuum for 4 hr at 150°C and then overnight at 400°C . In at least two cases there was evidence that the disulfide (SnS_2) had formed during chemical preparation as indicated by the appearance of yellow-gold plates. The SnS_2 was converted to SnS by heating at 700°C under vacuum in a quartz reactor.

¹²Ibid, pp. 75-6.

In the most recently completed separation series for tin (MQ), all isotopes were collected, but the isotope of primary interest was ^{112}Sn . In previous collections using SnCl_4 as charge material, retention of ^{112}Sn in the receiver pocket was 24.9% and the product assay showed 70.05% ^{112}Sn ; the change to SnS as charge material resulted in better retention (71.7%) and the assay was increased to 79.6% ^{112}Sn .

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