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Preparation and Recovery of Cesium Compounds for Density Gradient Solutions[1]

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DISCLAIMER

SUMMARY

Methods and systems have been developed for purification, recovery and preparation of cesium compounds suitable for application to biological zonal centrifugation separations. Saturated solutions of cesium chloride with optical densities as low as 0.03 (1 cm. path at 260 mμ) have been prepared. Serum and other organic impurities are removed by carbonization and filtering. A liquid exchange system was designed for recovering high purity cesium compounds from impure solutions. In the simple semi-continuous system the cesium is selectively extracted from metallic impurities, including other alkali metals, with 4-sec-butyl-2-(α-methylbenzyl)-phenol in Varsol from an alkaline solution, and stripped with acid.

High purity cesium compounds have been used in preparing density gradients for isolating viruses, subcellular fractions and nucleic acids by zonal centrifugation (1). To prevent harmful effects, the total divalent cation impurities should be less than 100 ppm. and total elemental impurities ~~are~~ should not to exceed 1%. Since optical methods are used to monitor the centrifugation separations for particle bands, the optical density at 260 mμ of the saturated solutions must be low, preferably less than 0.1 for a 1 cm. light path.

This report describes methods developed for improving the optical density of cesium chloride, recovering high purity cesium compounds from waste solutions, and preparing organic cesium salts.

IMPROVING THE OPTICAL DENSITY OF CESIUM CHLORIDE

The optical density at 260 mμ of the effluent solutions from the zonal centrifuge is monitored to detect and measure particle bands. For best sensitivity and resolution, solutions with a low optical density are desired. The optical density (1 cm. path at 260 mμ) of a saturated solution of purified cesium chloride, purchased from American Potash and Chemical Corporation, was 0.32. Repeated filtration of the solution through Whatman No. 42 paper lowered the optical density to about 0.2.

A simple treatment was developed for improving the optical (and chemical) quality of new cesium chloride. In the procedure the dry salt is heated to 450-470°C. for 30 minutes. The salt is then cooled and enough distilled water is added to make a saturated solution, which is filtered. Trace organic impurities are destroyed and certain trace metals including iron, calcium, and aluminum are removed as oxides or hydrated oxides. Saturated solutions with an optical density as low as 0.03 were prepared in this manner.

RECOVERY OF WASTE CESIUM CHLORIDE

Waste solutions are autoclaved twice before handling, to ensure that virus contaminants are inactivated.

Organic and inorganic impurities are introduced in the zonal centrifugation program. Sucrose is used in some experiments. Viruses are added to the gradient solutions in serum cultures. A number of anionic and metallic impurities enter the system from these additives. Others come in from trace erosion and corrosion of the metallic machinery. Most of these impurities must be removed regularly from the waste cesium chloride. Divalent metals, as well as organic contaminants, need to be removed after each usage.

Since alkali metals are introduced in only small quantities by the serum, and since fractional percentages of these metals are permissable, several use-cycles are possible before their removal is necessary.

Carbonization-Filtration Removal of Serum and Certain Metals

Waste cesium chloride solutions are evaporated to dryness in 5-liter boiling flasks, using Glas-Col heaters. The solids, including organic contaminants, are heated at 450 to 500°C. for 2 hours. This operation degrades the organic materials to carbon which is subsequently removed by filtering through a bed of filter pulp and decolorizing carbon on a Whatman No. 42 filter paper. Some of the metallic impurities are removed as hydroxides or oxides and by sorption on the carbon during the filtering process.

The average optical density of saturated solutions of cesium chloride recovered in this way is less than 0.05. Chemical and spectrochemical analyses of recovered cesium chloride are presented in table I. Metallic impurities, except sodium and potassium, were not detected.

Removal of Metallic Impurities Including Alkali Metals

BAMBP Extraction. An organic extraction method (2) developed at the Oak Ridge National Laboratory is used for removing metallic impurities. In this method cesium is separated by liquid cation exchange with 4-sec-butyl-2-(α-methylbenzyl)-phenol, conveniently called BAMBP.

A Varsol solution of BAMBP, in the hydrogen form (ROH), is reacted with the impure cesium chloride solution, made alkaline with sodium hydroxide:

$$ROH + Cs^+ + OH^- \longrightarrow ROCs + H_2O$$

The phenolic BAMBP is a weak acid, so that cesium extraction is sensitive to pH and best at higher pH values. The extractant has more affinity for cesium than for sodium or other metals of interest. According to Arnold and Crouse (3), at pH 12 to 13 the order of extractability is $Cs > Rb > K > Na > Li$. In this pH region, separation factors as high as 250 for cesium/potassium and several thousand for cesium/sodium are found, depending on the concentrations involved. Under usual process conditions, a maximum solvent loading of one mole of cesium per 4 moles of the substituted phenol is attained. According to Egan et al. (4), additional molecules of the phenol are tied up in solvating the salt molecule in the organic phase.

TABLE I

ANALYSIS OF CESIUM CHLORIDE AFTER CARBONIZATION-FILTRATION RECOVERY

Spectrochemical		Chemical	
Element	Concentration of Each Element, ppm.*	Measurement	Concentration*
Ag, Al, Be, Ca, Cr, Cu, Fe, Mg, Mn, Mo, and V	< 1	CsCl	1,242 g./l.
Pb and Ti	< 5	P as PO_4^{-3} (colorimetric)	< 5 ppm.
Bi, Cd, Co, Ni, Si, and Sn	<10	Nitrogen (Kjeldahl)	<25 ppm.
P and Zn	<50	Density	1.91 g./ml.
Na (flame photometry)	500	Optical Density at 260 mμ vs. H_2O	0.047
K (flame photometry)	80		

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* The symbol "<" means "less than" and denotes the lower limit of detection; ppm. values are on a cesium chloride (weight) basis.

The cesium is stripped from the organic phase with dilute hydrochloric acid:

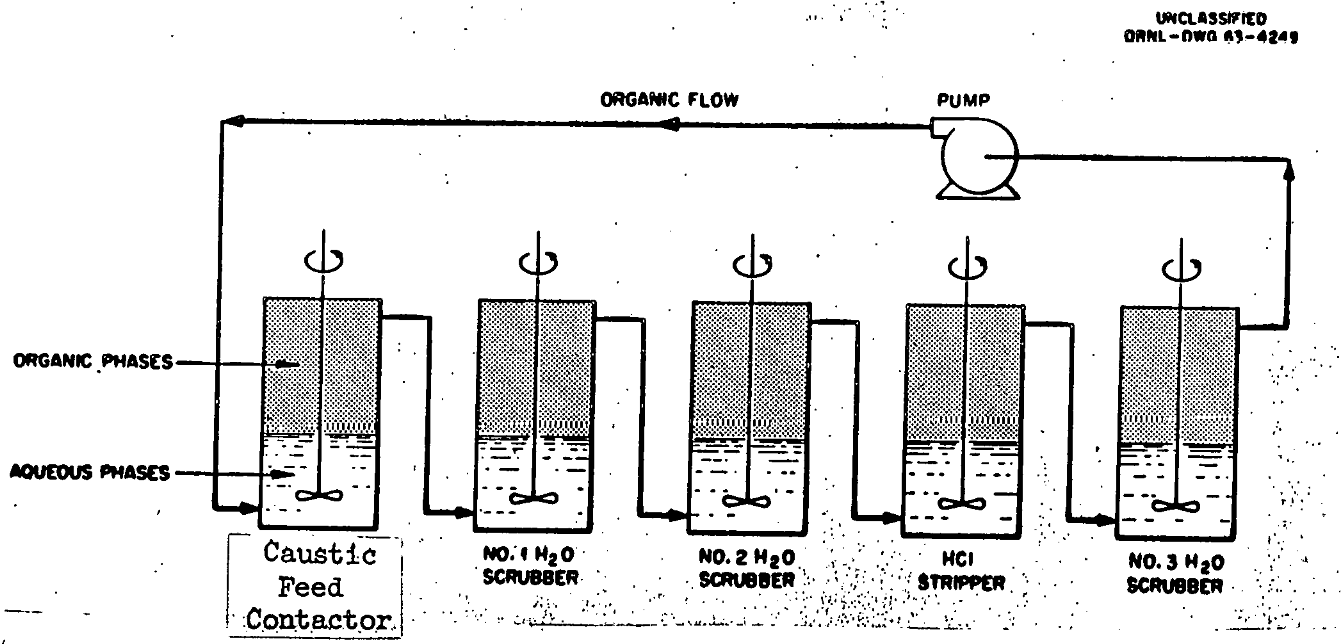
$$ROCs + H^+ + Cl^- \longrightarrow ROH + Cs^+ + Cl^-$$

Thus, cesium is preferentially transferred from the alkaline feed solution, through the organic phase, to the acid strip solution. The strip system regenerates the BAMBP to the hydrogen form in the recycling organic phase. Other metals are excluded from the product solution by scrubbing the loaded BAMBP with water prior to stripping. The water effectively removes metals which are held less firmly than cesium.

Laboratory Tests and Results

The experimental laboratory scale system (text-figure 1) consisted of the feed contactor, two water scrubbers, the hydrochloric acid stripper and a third water scrubber. A solution of BAMBP (1 molar) in Varsol was circulated through the static aqueous phases with a small centrifugal pump. For each mole of cesium chloride being processed, one mole of sodium hydroxide was added to the feed contactor and one mole of hydrochloric acid was added to the stripper. A slight excess of the acid and base reagents was required for complete cesium transfer. Because of the small quantity of BAMBP available at the time of this test, the scale of the studies was limited to 600 ml. volume contactors.

Legend for Text-Figure 1.—Laboratory system for recovering cesium chloride from impure solutions. The circulating organic phase transfers cesium from the caustic feed contactor to the acid stripper. Purpose of the water scrubbers is to prevent other metals from reaching the stripper.



Text-figure 1

Results of a cesium extraction test, where the organic phase was circulated at 100 ml./min. for 45 minutes, are presented in table II. Cesium removal from the feed was 99.8%; about 10% of the original cesium remained in the scrubbers and the organic phase, according to the final cesium concentration in the stripper. The cesium remaining in the system, of course, was recovered in subsequent runs. The product recovered in the stripper was better than 99.9% pure. The product solution was evaporated to dryness, dissolved in water, and filtered. The optical density of the saturated filtrate was 0.31.

The carbonization procedure, described earlier, would probably have improved the optical density.

PROTOTYPE EXTRACTION SYSTEM

A prototype production-scale liquid exchange system was designed and tested. The system, shown in figure 1, consisted of five Plexiglas contactor stages. In each stage, hollow glass centrifugal stirrers disperse the organic into the aqueous phase as shown in text-figure 2. A differential organic level is developed between the outer and inner compartments of adjacent contactors, effecting transfer of the organic phase without the use of external pumps. The organic-aqueous interface serves as a seal to prevent back-mixing.

Legend for Text-Figure 2.—Schematic of flow within contactor of cesium recovery system. The plastic and glass construction eliminates contamination problems.

TABLE II

TEST DATA FROM LABORATORY BAMBP EXTRACTION SYSTEM FOR REPROCESSING CESIUM CHLORIDE

	Organic Volume (ml)	Aqueous Volume (ml)	Concentration (g/liter)[a]					Normality		
			CsCl	Na	K	Ca	Mg	Cs^+	OH^-	HCl
Extractor										
Initial	330	250	112.1	21.0[b]	0.1	0.07[c]	0.003[c]	0.666	0.86	
Final	330	250	0.25	Strong	0.1	0.001[c]	0.00005	0.0015	0.06	
No. 1 Scrubber										
Final	455	125	1.1	0.25	0.01	0.02	0.0002		0.015	
No. 2 Scrubber										
Final	455	125	3.0	0.11	0.04	0.01	0.0003		0.012	
Stripper										
Initial	330	250	0	0	0	0	0	0	0	0.875
Final	330	250	101.3	0.03	0.005	0.002	0.0001	0.602		0.19
No. 3 Scrubber										
Final	330	250	1.5	0.006	0.001	0.00076	0.00015			

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[a] Aqueous.

[b] As NaOH and NaCl.

[c] Prior to filtering where some Mg and Ca was removed.

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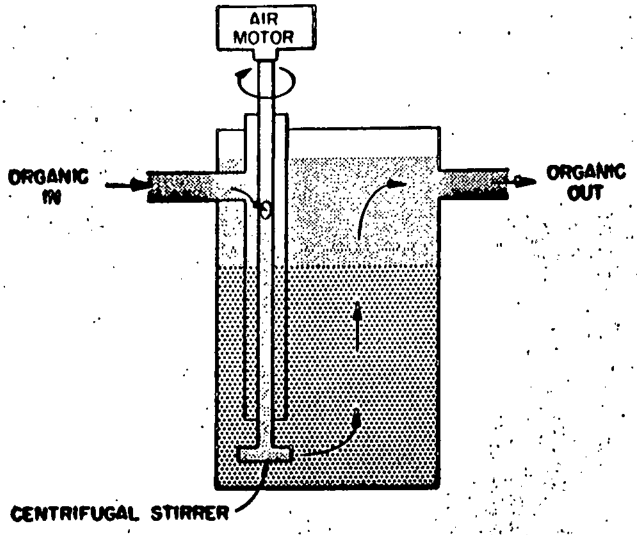

Text-figure 2

Demonstration Run

A demonstration purification run was made with 4 lbs. of cesium chloride spiked with 500 ppm. each (CsCl basis) of Al^{+3}, Fe^{+2}, Cu^{+2}, Ni^{+2}, Zn^{+2}, Cd^{+2}, Cr^{+6}, Co^{+2}, Mg^{+2}, Ca^{+2}, Ba^{+2}, Sr^{+2}, Li^{+1}, NH_4^{+1}, and PO_4^{-3}. Also added was 1.4% NO_3^{-1}, 0.15% SO_4^{-2}, 0.5% K^{+1}, and a total of 2.7 lbs. of sodium as the chloride and hydroxide. Some of the sodium hydroxide was added during the extraction.

The basic solution was filtered prior to extraction, removing some of the metal impurities. Thirty-four liters of 1 molar BAMBP in Varsol was used, and each scrubber and stripper contained an aqueous phase of 6.7 liters.

Production rates were limited by persistent emulsion formation in the scrub stages. Addition of cesium chloride to these stages, as an emulsion breaker, reduced (but did not eliminate) the problem. Contributing to, and possibly responsible for, the emulsion problem was the slow erosion of the Plexiglas components of the system by the organic extractant. Connecting tubing was polyethylene, which was not attacked. Current plans include tests with a system constructed entirely of polyethylene, similar in design to the Plexiglas system.

The BAMBP extraction system was operated with organic flow rates up to about 800 cc. per minute and production rates as high as 2.5 lbs. of cesium chloride per hour. The cesium chloride product was very pure. Except for 170 ppm. sodium (cesium chloride basis), no detectable metallic impurities were found (see table I for limits of detection).

PREPARATION OF ORGANIC COMPOUNDS OF CESIUM

The prototype extraction system was conveniently applied to the preparation of urgently needed organic cesium salts. By using cesium chloride solution as the feed and substituting the appropriate organic acid in the stripper, solutions of high purity cesium tartrate and citrate were produced. Decolorizing carbon was used to remove traces of the extractant from the final product. The levels of impurities in these salt solutions were comparable to those shown in table I.

DISCUSSION

The high cost of pure cesium compounds suggests that methods for recovering this material be devised. Based on previous studies concerned with the purification of radioactive cesium, a separation methods has been developed which allows cesium to be recovered as either an inorganic or an organic salt from solutions contaminated with alkali or heavy metals, or organic compounds. The high speed, high capacity rotors now under development for studies on DNA banded in cesium chloride or sulphate will require as much as one kilogram of cesium salt per experiment. It will not be feasible to test or use such rotors in the absence of simple methods for recovering cesium in a high state of purity.

LEGEND FOR FIGURE

Figure 1. Production-scale cesium recovery system. Containers are Plexiglas.

Plate

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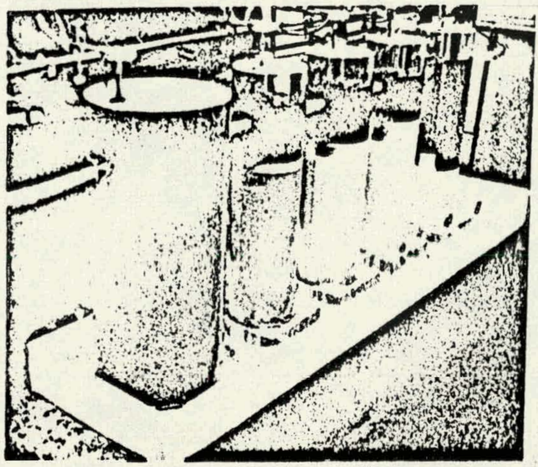

Figure 1. Production-scale cesium recovery system. Containers are Plexiglas.

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