313
3-30-66

RFP-691

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

MASTER

LIQUID MEDIA FOR DENSITY MEASUREMENTS
OF BERYLLIUM, PLUTONIUM, AND URANIUM

by

H. N. Elsheimer

THE DOW CHEMICAL COMPANY
ROCKY FLATS DIVISION
P. O. BOX 888
GOLDEN, COLORADO 80402
U. S. ATOMIC ENERGY COMMISSION
CONTRACT AT(29-1)-1106

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Printed in USA. Price \$2. Available from the Clearinghouse for Federal Scientific and Technical Information, National Bureau of Standards,
U. S. Department of Commerce, Springfield, Virginia

25 February 1966

RFP-691

UC-2 GENERAL, MISCELLANEOUS,
AND PROGRESS REPORTS

TID-4500 (47th Ed.)

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

LIQUID MEDIA FOR DENSITY MEASUREMENTS
OF BERYLLIUM, PLUTONIUM, AND URANIUM

by

H. N. Elsheimer

THE DOW CHEMICAL COMPANY
ROCKY FLATS DIVISION
P. O. BOX 888
GOLDEN, COLORADO 80402
U. S. ATOMIC ENERGY COMMISSION
CONTRACT AT(29-1)-1106

A C K N O W L E D G E M E N T S

We wish to thank J. D. Livingston, J. L. Holst, D. S. Irwin, and J. E. Hill for their helpful counsel in our evaluation studies. We are also indebted to K. V. Best, D. N. Taylor, and R. E. Martindale for their cooperation in evaluating the usefulness of Freon-113^{®*} as a density medium, and to Dr. J. T. Byrne for the initial suggestion regarding the "Freon" fluorocarbon compounds as potentially suitable density immersion media.

^{®*} - E. I. duPont de Nemours & Co.

C O N T E N T S

	Page
Acknowledgements	ii
Abstract	iv
Summary	v
INTRODUCTION	1
General	1
Density Measurements	1
Beryllium	2
Uranium and Plutonium	2
EXPERIMENTAL (LITERATURE SURVEY)	3
Preliminary Considerations	3
Toxicity	4
Surface Tension and Flammability	5
Chemical and Radiation Stability	5
Preparation of Tables	5
RESULTS	7
Experimental Studies on "Freon-113"	8
DISCUSSION	9
Beryllium	9
Uranium and Plutonium	12
RECOMMENDATIONS	17
Beryllium	17
Uranium and Plutonium	19

A B S T R A C T

An extensive literature survey was conducted to ascertain the optimum liquid media for determining the densities of beryllium, uranium, and plutonium. In conjunction with the literature survey, a limited amount of experimental work was done with "Freon-113" fluorocarbon, a potentially useful immersion liquid for all three types of metals, especially beryllium. Successful application has since been made of this particular compound for not only beryllium, but also plutonium.

S U M M A R Y

A literature survey was conducted in order to ascertain suitable media for measuring the densities of beryllium, plutonium, and uranium. High preference was given to density media with a density close to, but less than, 1.8 for beryllium and as high as possible for uranium and plutonium.

Other than density, the key factors considered were:

- 1 cost,
- 2 degree of purity,
- 3 vapor pressure,
- 4 flammability,
- 5 surface tension,
- 6 toxicity,
- 7 chemical stability, and
- 8 radiation stability (uranium and plutonium only).

The best choice for beryllium on the basis of present knowledge is "Freon-113" 1,1,2-trichlorotrifluoroethane. The feasibility of this compound as a density immersion medium was evaluated favorably by the Rocky Flats Mass Standards Laboratory on the basis of a limited amount of experimental work.⁽¹⁾ This solvent was put into use at Rocky Flats as a medium for density measurements of beryllium in January 1964, and has since given very satisfactory results.

The best choices, exclusive of cost, for uranium and plutonium would seem to be 1,1,2-tribromoethene and 1,2-dibromoethene. Apart from these, 1,1,2-tribromoethane and 1-octanol are secondary choices. Monobromobenzene is definitely not a highly satisfactory choice for either uranium or plutonium, and especially not for uranium due to its high toxicity and its objectionable odor. The "Freon-113" fluorocarbon is another possibility despite its low volatility, chiefly due to its low corrosive character with regard to plutonium. As of August 1965, the density of plutonium at Rocky Flats has been measured in "Freon-113".

(1) J. D. Livingston, private communication.

I N T R O D U C T I O N

GENERAL

This literature survey was made at the request of the Metal Production Group at Rocky Flats which was interested in an evaluation of optimum immersion media for beryllium, uranium, and plutonium. At the time of the request, monobromobenzene was being used for density measurements of plutonium and water for uranium, but beryllium densities were not being measured at Rocky Flats.

Since the densities of plutonium and uranium are of the same order of magnitude and these metals require similar handling, potential immersion liquids for them were considered a single entity and constitute a major division in certain sections of this report. Potential immersion liquids for beryllium constitute the other main division in these same sections.

Tables of the best choices for each type of density media are contained in this report, plus an evaluation of these choices and a recommendation for the best choices in each case on the basis of present knowledge. The gaps in knowledge are such that an experimental study is recommended in the case of density media for uranium and plutonium.

DENSITY MEASUREMENTS

The method employed at Rocky Flats for density measurements is a hydrostatic weighing method. This is done by attaching one end of a wire to one arm of an equal-arm balance and the other end of the wire to a metal basket in which the metal is placed. The wire must pass through the surface of the liquid with the basket attached in taking the balance reading before the metal is added to the basket. Thus, errors due to the weight of this attachment and surface tension of the liquid on the suspension wire are avoided.

The density of the solid material is calculated from the weight in air of the part divided by its volume. This is equivalent to multiplying the weight in air by the density of the liquid at the temperature of

observation and dividing by the difference between the weight in air and the weight of the solid in the immersion liquid.

BERYLLIUM

The primary objective of this two-part study was to find a suitable liquid medium for determining the density of beryllium. The density of beryllium is about 1.849 and, ideally, the density of the immersion liquid should be slightly less than this value. This would enhance the precision of the method.

Other characteristics sought for in a suitable density measuring liquid for beryllium were a low temperature coefficient, a linear temperature-density relationship, chemical inertness toward the solid material, low volatility, a low surface tension so that wetting of the metal would be enhanced, nonflammability, and low toxicity. Also, there should be little or no residue left on the solid after determining its weight in the liquid. A suitable density medium would not be an oil, for example. The degree of volatility, with reference to any toxicity of a given density measuring immersion liquid, would determine the need for and extent of provision for venting any solvent vapors away from the weighing area. This introduces the criteria of cost, both in terms of the immersion liquid itself and of any special equipment necessary for venting vapors away from it.

URANIUM AND PLUTONIUM

It was requested that it be ascertained whether monobromobenzene is the ideal density measuring medium for plutonium, and to find a suitable replacement for water as a medium for uranium. Water is deleterious to uranium in that both radiolysis and corrosion occur; hence, the dissatisfaction with water as a density medium for uranium. Important factors for plutonium and uranium, which did not apply in the case of beryllium, were a density as high as practicable and radiation stability.

The fact that the density of the metal would be measured in a glovebox, or hood, meant that any tendency toward volatility would be aggravated by negative pressure maintained in the box or hood. Most of the other

factors still applied, such as low surface tension for purposes of wetting the metal, ease of removal of the immersion liquid from the metal, low temperature coefficient, chemical inertness, nonflammability, purity, cost, and low toxicity. The latter is not so important in a glovebox situation since the analyst would not inhale the vapors, unless the vapors were of such a nature as to attack the rubber gaskets and gloves.

EXPERIMENTAL (LITERATURE SURVEY)

PRELIMINARY CONSIDERATIONS

The literature survey began with a search of the chemistry handbooks (2,3) for liquids which have a density slightly less than that of beryllium and as high as possible relative to plutonium and uranium. High-boiling liquids were also desirable.

Starting with the above-mentioned list, the purity, cost, and commercial availability of these compounds were ascertained from data in available chemical catalogs. (4,5) Those compounds not available in pure form were eliminated immediately. Compounds with an exorbitant cost were either eliminated or considered secondary choices. The remaining compounds were grouped into two lists of approximately 10 each on the basis of intended usage. Two types of "Freon" fluorocarbon compounds were also included in the beryllium list because of their potentially desirable properties. Monobromobenzene, "Freon-113" trichlorotrifluoroethane, and 1-octanol were added to the plutonium and uranium list. Monobromobenzene was included because of its usage

(2) Handbook of Chemistry and Physics, 44th Ed., Chemical Rubber Publishing Company, 1962-63.

(3) Lange's Handbook of Chemistry, 9th Ed., Handbook Publishers, Inc., 1956.

(4) Fisher Chemical Index, Catalog 123, Fisher Scientific Co., 1959.

(5) Eastman Organic Chemicals, 42nd Ed., Distillation Products Industries, Eastman Organic Chemicals Dept., 1960.

for plutonium at Rocky Flats until recently, "Freon-113" because of low corrosion toxicity properties, and 1-octanol because of its previous use for uranium at Hanford.⁽⁶⁾

TOXICITY

Toxicity was one of the more important items considered in both groups of compounds and an extensive search of several pertinent volumes was made.⁽⁷⁻¹³⁾ The latter reference⁽¹³⁾ was particularly helpful since it evaluated halogenated hydrocarbons as to type, according to degree of saturation, and gave available data, including permissible limits, for a large number of chloro analogues to the bromo compounds under consideration. The Industrial Hygiene Department at Rocky Flats was consulted about many compounds for which no specific toxicity data was found. The net result was the realization that factual information on the toxicity of a good number of compounds under consideration could only be inferred by analogy.

The factor of toxicity was considered most important in the case of beryllium where the work would presumably be done in an open hood. Density measurements on plutonium and uranium can be done either in a glovebox or an open-faced "B" box or hood.

(6) Mallett, G. R., Density Determinations for Radioactive Materials, Hanford Atomic Products Operations, 1954, AEC Report HW-34079 (rev.).

(7) Sax, N. I., Dangerous Properties of Industrial Materials, New York, Reinhold Publishing Corp., 1957.

(8) Fairhall, L. T., Industrial Toxicology, Baltimore, The Williams and Wilkins Co., 1949.

(9) Spector, W. S., Handbook of Toxicology, Philadelphia, W. B. Saunders Co., 1956, Vol I.

(10) Schefflan, L. S. and Jacobs, M. B., The Handbook of Solvents, New York, D. Van Nostrand Co., 1953.

(11) Mellan, I., Sourcebook of Industrial Solvents, Halogenated Hydrocarbons, New York, Reinhold Publishing Co., 1957, Vol II.

(12) Mellan, I., Industrial Solvents, 2nd ed., New York, Reinhold Publishing Corp., 1950, pp 210-13.

(13) Patty, F. A., Industrial Hygiene and Toxicology, New York, Interscience Publishers, 1949, Vol II, pp 775-8, 791, 825, 853, 899.

SURFACE TENSION AND FLAMMABILITY

Data on the surface tension as a clue to wetting ability and flammability or flashpoint were taken from various sources, none of which were sufficiently extensive. (7,10,11,14) Again, inferences can only be drawn in several cases from analogous compounds.

CHEMICAL AND RADIATION STABILITY

Two other areas of concern were chemical stability (i.e., the tendency to react with the part material) and radiation stability. The latter obviously was of concern only with potential density media for uranium and plutonium. Since these are related properties, a table of bond strengths for various simple types of hydrocarbons and halogenated hydrocarbons was consulted and both the average total bond strength of the compound and the average strength of the bonds of the functional group or groups attacked was estimated. (15)

Another reference was specifically concerned with radiation effects on organic compounds and materials. (16) A section pertaining to radiation effects on pure compounds discusses and illustrates by tables of data trends in various groups of materials. Mechanisms are postulated and the effect of structure, experimental variables, and additives discussed. The information on trends was particularly helpful to this study.

PREPARATION OF TABLES

As a final step, Tables I and II were prepared for the two groups of immersion liquids and the order of preference of the density media

(7) loc. cit., p. 4.

(10) loc. cit., p. 4.

(11) loc. cit., p. 4.

(14) International Critical Tables of Numerical Data, Physics, Chemistry, and Technology, New York, McGraw-Hill Book Co., 1933, VOLS III and IV.

(15) Morrison, R. T. and Boyd, R. N., Organic Chemistry, Boston, Allyn and Bacon, Inc., 1959, p 16.

(16) Bolt, R. O. and Carroll, J. G., Radiation Effects on Organic Materials, New York, Academic Press, 1963, pp 90-97, 111-118.

TABLE I

POTENTIAL DENSITY SOLVENTS FOR BERYLLIUM

Type of Compound	Density	Boiling Point (°C)	Relative Chemical Stability*	Surface Tension (Dynes/cm)	Probable Toxicity** (Relative)	Cost (Approx.)	Order of Choice
"Freon-113"	1.553 30°	47.6	1	19.6	1	\$400/55 gal.	1
"Freon-112"	1.634 30°	92.8	1	23.0 86° F	1	Unknown	
2-bromoethanol	1.7720 20°/4	150.3	3	-	4	\$17.45/500 g.	2
1-iodopropane	1.743 20°/4	102.4	5	20.0 102.5° C	8	\$9.80/500 g.	
2-iodopropane	1.703 20°/4	88.90	6	19.5 89° C	8	\$12.30/500 g.	
1,2-dibromo, 2-methylpropane	1.759	149	4	-	5	\$19.85/500 g.	4
Isoamyl iodide	1.515 18°/4	148	8	-	6	\$19.75/500 g.	
Amyl iodide	1.517 20°/4	152.55	7	-	0	\$18.50/500 g.	
1-iodobutane	1.617	131	6	-	7	\$12.60/500 g.	
1-bromo, 2-chloroethane	1.689 19°/4	104-106	3	-	0	\$5.50/500 g.	3
2-bromoethyl acetate	1.514 20°/4	160-61	?	-	2	\$20.90/500 g.	
1-bromo, 4-fluorobenzene	1.593 15°	152-5	2	29.4 70° C	3	\$38/500 g.	5

* Based on bond strength of halogen substituents and structure. Numbered in the order of decreasing stability. (15)

** Numbered in the order of increasing toxicity.

(15) loc. cit., p 5.

TABLE II

POTENTIAL DENSITY SOLVENTS FOR URANIUM AND PLUTONIUM

Type of Compound	Density	Boiling Point (°C)	Relative Radiation Stability*	Surface Tension (Dynes/cm)	Probable Toxicity** (Relative)	Cost (Approx.)	Order of Choice
1,1,2-tri bromoethane	2.579 20°/4	188.4	4	-	4	\$23/500 g.	2
1,1,2-tri bromoethene	2.708 20.5°	163-4	1	-	2	\$40/500 g.	1
1,2-dibromo-ethene	2.267 17.5°/4	108	1	-	2	\$36.50/500 g.	1
Methylene bromide	2.4953 20°/4	98.2	2	-	4	\$3.20/500 g.	5
Ethyl iodide	1.933 20°/4	72.2	8	29.4 20°	3	\$15/500 g.	7
1,2-dibromo-propane	1.9333 20°/4	139-141	5	21.2 141.5°	4	\$8.20/500 g.	3
1,3-dibromo-propane	1.979 20°/4	163-7	3	-	4	\$29/500 g.	3
1,2,3-tri-bromopropane	2.436 23°	220	6	45.36 20°	4	\$14.90/500 g.	3
2,3-dibromo-propanol	2.1259 25°	118 17mm	7	-	5	\$9.85/500 g.	6
1-octanol	0.829 20°/4	194.5	2	-	1	\$2.50/500 g.	2
Monobromo-benzene	1.495 20°/4	155-7	2	36.5 20°	6	\$3.50/500 g.	4

* Based on bond strength of halogen or other substituents and structure. Numbered in the order of decreasing stability.

** Numbered in the order of increasing toxicity.

listed. Items included in both tables were density, boiling point, surface tension, cost, estimated relative toxicity, chemical stability (in the case of the prospective beryllium density immersion liquids), and radiation stability (in the case of the prospective uranium and plutonium density immersion liquids).

The various facets of data were not necessarily weighted equally in arriving at an order of choice. For example, toxicity was a more important consideration for a potential beryllium density medium, while radiation stability was considered important for a potential uranium-plutonium density medium. For the purpose of making a choice, cost was not necessarily considered a highly significant item. Our reasoning here was that the cost of bulk quantities (prices were not generally available) would probably not be reduced to the same extent for all items. Also, the ultimate decision as to what would be economically feasible rests with the user and must be evaluated in terms of estimated overall costs for a given period of time.

R E S U L T S

A summary of the data pertaining to beryllium is presented in Table I. Data pertaining to uranium and plutonium are given in Table II. Listed in Table III are some statistical data based on actual usage of "Freon-113" fluorocarbon as a density immersion medium for beryllium at Rocky Flats.

TABLE III

BERYLLIUM DENSITY MEASUREMENTS USING
"FREON-113" AS A LIQUID IMMERSION MEDIUM

<u>Operator</u>	<u>Measurement</u>	<u>Sample 1</u>	<u>Sample 2</u>	<u>Sample 3</u>
A	1	0	1	2
	2	2	1	1
	3	3	1	2
B	1	2	1	2
	2	2	1	2
	3	2	1	2
C	1	1	2	3
	2	0	1	4
	3	0	0	2

NOTE: These values represent density values minus the constant 1.849 and multiplied by 10^3 .

EXPERIMENTAL STUDIES ON "FREON-113"

Since "Freon-113" seemed so promising as a density-measuring medium, and quantities of it were available, some experimental tests were made by the Mass Standards Laboratory.⁽¹⁾ The following observations were made:

- 1 The precision obtainable for a temperature-density curve is similar to that obtainable for monobromobenzene; namely, ± 0.0005 g/cc. Techniques followed were those employed for other density mediums, such as monobromobenzene.
- 2 The temperature stability of the compound is a critical factor in that a small change in the environmental temperature produces an immediate change in the temperature of the immersion liquid.
- 3 The evaporation rate is quite high, being 1.7 times that of carbon tetrachloride.⁽¹⁷⁾ This means that the density measurements should be carried out in a minimum of time, the bath containing the liquid should be covered tightly when not in use, and the liquid must be consistently pure. Significant changes in liquid level during the course of a measurement may lead to a significant error.
- 4 Surface tension and viscosity were satisfactory.
- 5 The odor was not objectionable.

As a consequence of the above data and the preliminary recommendations of this report, facilities were designed and "Freon-113" fluorocarbon put into use as the density medium for beryllium at Rocky Flats. Statistical evaluation by a random block design of a typical set of data shown in Table III elicited the following conclusions:

- 1 There was no significant difference between operators.
- 2 The largest variance was between samples.

(1) loc. cit., p iv.

(17) Solvent Properties Comparison Chart, E. I. du Pont de Nemours & Co., Freon Products Division, 1959, Freon Technical Bulletin FS-6.

- 3 The overall measurement capability of the system is ± 0.003 g/cc at the 95-percent confidence level on the basis of this particular set of data only.

D I S C U S S I O N

BERYLLIUM

Toxicity Considerations

One of the more important factors in evaluating a potential density medium for beryllium is the toxicity or health hazard. In speaking of the toxic hazards for a solvent, reference is made to the vapor concentration to which workers would be exposed rather than accidents involving swallowing of the liquid or skin contamination. This has been defined as "the upper limit of concentration of a contaminant in the air which will not cause injury to an individual exposed continuously during the working day and for indefinite periods of time."⁽¹²⁾

The health or toxicity hazard of a given chemical solvent or liquid may be divided into two categories; namely, its narcotic effect and its toxic effect. In general, there is a decrease in narcotic action and an increase in toxic action with an increase in molecular weight and boiling point within a given series of compounds, such as the halogenated methanes, ethanes, and propanes.⁽¹³⁾ Thus, a bromo-substituted compound is more toxic than a chloro, and an iodo more than a bromo. Also, the more highly substituted a given compound is with halogen groups, the more toxic it is, except that if "delayed" deaths are taken into account (deaths from prolonged exposure over a period of time), this is not strictly true and there is no predictable pattern.⁽¹³⁾ Fluoro-substituted compounds are an exception to these rules and usually the more highly substituted with fluorine atoms, the less toxic the compound relative to its other halogen derivatives.⁽¹³⁾ Hence, one reason for the low toxicity of the "Freon" fluorocarbon compounds.

(12) loc. cit., p 4.

(13) loc. cit., p 4.

The mono and dichlorinated benzenes have strong narcotic effects and cause moderate respiratory irritation⁽¹³⁾, so it is to be expected that the bromo derivative would be more irritating to the respiratory tract. Conversely, the fluorine atom on the single aromatic compound listed would reduce its toxicity.

The toxicity of many compounds can only be inferred, as most available information on maximum dosage is for chlorinated hydrocarbons. One can generalize, however, as has been suggested earlier, and make the following hypotheses:

- 1 The most chemically active halogenated hydrocarbons will be the most toxic.
- 2 The iodo compounds will be the most toxic of the halogenated hydrocarbons for a given series of analogous compounds.

Hence, the listed iodo compounds are the poorer choices as regards their relative toxicity.

"Freon" Fluorocarbon Compounds

The desirability of "Freon" fluorocarbon compounds lies in their very low toxicity, nonflammability, excellent thermal and chemical stability, low viscosity and surface tension, and high degree of purity.^(18,19)

One aspect of their purity is that no inhibitors are necessary due to their high degree of chemical stability. Their cost is relatively high, but their good features seem to be commensurate to the cost.

The "Freon-112" fluorocarbon was not included as a desirable choice since it is not a liquid at room temperature. Thus, a constant-temperature bath or box would be required which would operate at a temperature several degrees above room temperature. The extra expense and inconvenience might be prohibitive.

(13) loc. cit., p 4.

(18) Properties and Applications of the "Freon" Fluorinated Hydrocarbons, E. I. du Pont de Nemours & Co., Freon Products Division, 1957, Freon Technical Bulletin B-2.

(19) Freon Fluorocarbon Solvents, E. I. du Pont de Nemours & Co., Freon Products Division, Freon Solvent Bulletin FS-1.

"Freon-113" has in the past been satisfactorily used to clean metal at Rocky Flats and leaves only slightly more residue than the currently-used cleaning solvent, trichloroethylene. As noted in the RESULTS, the chief disadvantages of "Freon-113" would seem to be its fairly high rate of evaporation and its cost. If suitable precautions are taken, however, the former can be minimized.

Approximately 18-months experience at Rocky Flats, utilizing "Freon-113" as a density medium for beryllium has satisfactorily demonstrated its value. The reproducibility of measurement is very good, in fact, better than postulated earlier, and its non-toxic character and lack of objectionable odor make it very desirable. These last factors make it possible to eliminate any expensive venting facilities.

Evaporation of the solvent is fairly rapid, but not such as to hinder the quality of the measurements, if made in a reasonable length of time. Excessive loss of solvent can be inhibited by tightly covering the solvent bath with either a friction-fitting cover or a cover equipped with clamps. Location of the bath should be such that there are not large fluctuations in air currents or, in bath temperatures.

Other Choices

From the standpoint of closeness of approach of their density to that of beryllium, 2-bromoethanol is the best choice with 1,2-dibromo, 2-methylpropane, and 1-iodopropane nearly as good choices. Their relative chemical stability is good, but not nearly as good as for the "Freon" fluorocarbon compounds, and their toxicity hazard is rather high. Ethylene chlorohydrin (2-chloroethanol) produces marked irritation of the respiratory tract, so it is to be expected that the toxicity of the 2-bromoethanol might well be such as to make it undesirable.

The other iodopropanes have reasonably high densities and boiling points and a moderate cost, but their toxicities and chemical stabilities would make them rather undesirable.

Ethylacetate has a high tolerance (600 ppm).⁽¹³⁾ It is postulated, therefore, that the bromo-derivative would be relatively safe to use.

The 1-bromo - 2-chloroethane compound is relatively cheap and has a high density and good chemical stability, but is rated as being fairly toxic by virtue of its bromo group.

The best features of 1-bromo - 4-fluorobenzene are its stability and relatively low toxicity. Its high cost and probably high surface tension at room temperature counteract these good features.

URANIUM AND PLUTONIUM

Density

In general, the density of a given solvent need not have a greater density than that of water, so long as the magnitude of the sample weight is sufficiently large (40 g. or more). This deduction is made from the relationship of the various components in the density expression:

$$D_s = \frac{W_a \times D_l}{W_a - W_l}$$

where: D_s = density of the sample

D_l = density of the immersion liquid at the temperature of measurement

W_a = weight of sample in air

W_l = weight of sample in immersion liquid.

If either W_a or $W_a - W_l$ are large, or conversely, when W_l is small in relation to W_a , the precision of the results will be enhanced. W_l is small in relation to W_a , either when a large sample is weighed or when the density of the immersion liquid is high.

Nevertheless, so as to minimize error under any circumstances, there is some advantage in having as dense a solvent as practicable relative to

(13) loc. cit., p 4.

the density of the material to be weighed. Since sample sizes and weights are not uniform, the compounds under consideration were chosen with this philosophy in mind.

Radiation Stability

Relevant to the matter of radiation stability for halogenated hydrocarbons, the C-X bond is preferentially ruptured, except for the C-F bond which is more stable than the C-C or C-H bonds.⁽¹⁶⁾ The greater the atomic weight of the halogen, the greater the tendency for the C-X bond to rupture. Where radiolysis occurs, the principal hydrocarbon produced (RH) is the one corresponding to the parent (RX). More unsaturates are produced than saturates and either halogen gas (X₂) or halogen acid (HX) may appear, depending on the identify of the halogen.⁽¹⁶⁾ The more stable the bonding structure, the lower the yield of radiolysis products for a given amount of radiation.

Toxicity

The same generalizations that were made in the beryllium section of our discussion, with regard to toxicity of the halogenated hydrocarbons, apply here.⁽¹³⁾ It is to be remembered also that toxicity should not be as significant a factor here because of the nature of the working conditions. Maximum practical limits were available only for certain chloro analogues. Piecing together miscellaneous information, however, it appears that the saturated ethanes are considerably more toxic than the unsaturated ethenes and that one could expect brominated ethanes to be slightly more toxic than propanes brominated to a similar extent. As evidence, we submit the following table (Table IV) compiled from two tables concerned with the toxicity of halocarbon compounds.⁽¹²⁾

Monochlorobenzene has a maximum permissible limit of only 75 ppm⁽¹³⁾, which means that the bromo derivative is indeed very toxic. The 1-octanol solvent should be very toxic according to the trend of alcohols with increasing chain length, but its low volatility should offset this

(16) loc. cit., p 5.

(13) loc. cit., p 4.

(12) loc. cit., p 4.

TABLE IV
RELATIVE TOXICITIES OF SOME HALOGENATED HYDROCARBONS

Compound	Max. Allowable Conc. (ppm)	Toxicity*
Methyl Chloride	500	0.20
Methyl Bromide	100	2.00
Ethyl Chloride	20,000	0.05
Ethyl Bromide	2,000	0.06
Vinyl Chloride	5,000	-
Methylene Chloride	288	0.11**
Chloroform	100	1.00
Carbon Tetrachloride	50	1.00
Trichloroethylene	200	0.50
Tetrachloroethylene	200	0.50
Tetrachloroethane	5	10.00

* Toxicity Relative to CCl_4 = 1.00 Based on Allowable Conc. for Prolonged Exposure (Conc. by Vol. of Air).

** Less accepted figure.

considerably and the possible hazard is very slight. Iso-propanol is considered very safe in usage⁽¹³⁾, but the dibromo substituted compound should be fairly toxic.

One would expect the iodide group to make ethyl iodide fairly toxic, but not as much as it would a longer chain hydrocarbon or as much as compounds with two or more bromide groups.

Methylene bromide is definitely a toxic compound, but its chloro analogue has a suggested maximum practical limit of 500 ppm.⁽¹³⁾ Hopefully, something on the order of 100 ppm is its practical limit. It should be pointed out, however, that its volatility would make it more dangerous than similarly toxic compounds of a less volatile nature. Methylene chloride, by comparison, is 1.47 times as volatile as carbon tetrachloride.⁽¹⁶⁾ Ethyl iodide is also rather volatile, which would put it in the questionable category from the point of view of an industrial hazard.

(13) loc. cit., p 4.

(16) loc. cit., p 5.

Surface Tension

Data were not available for the surface tension of over one-half the compounds. Since the surface tension value for 1,2,3-tribromopropane is not significantly greater than that for monobromobenzene, which is deemed satisfactory as regards its wetting properties towards plutonium, and the surface tension of 1,2-dibromopropane is approximately one-half that of the 1,2,3-derivative, the surface tension of the other liquids should not be prohibitively high.

Flammability

Data were available for only two of the compounds under investigation. Monobromobenzene has a flash point of 123.8°C (flash point = the minimum temperature at which a liquid gives off vapor sufficient to form a flammable mixture in contact with air).⁽²⁰⁾ The compound, 1,2-dibromopropane, is described as being nonflammable. In general, the greater the degree of halogenation of a given hydrocarbon, the less its tendency toward flammability.⁽²⁰⁾ Hence, only ethyl iodide and methylene bromide would be suspect.

Ethene Compounds

As can be seen from Table II, 1,1,2-tribromoethene and 1,2-dibromoethene would be clear-cut first choices except for their cost. Their apparent relatively high radiation stability and relatively low toxicity are their best features, plus the high density and boiling point for the first-named compound. As is pointed out in the RECOMMENDATIONS, their cost is not necessarily prohibitive.

Other Choices

A probable high-working toxicity due to relatively high vapor pressure eliminates methylene bromide as a serious consideration for uranium parts, although its very low cost is appealing and it could conceivably

(20) Patty, F. A., Industrial Hygiene and Toxicology, General Principles, 2nd rev. ed., New York, Interscience Publishers, 1958, Vol I, pp 524, 542-4.

be used as a density medium for plutonium parts in a gloved-box arrangement. Ethyl iodide has too low an estimated radiation stability, as does probably 2,3-dibromopropanol. The gradation in stability between the latter compound and 1,3-dibromopropane, however, is not very large. Considering cost as a major factor, the bromopropanes, 1,1,2-tribromoethane, and 1-octanol rank as high choices.

Monobromobenzene and 1-Octanol

Monobromobenzene and 1-octanol are included as possibilities, despite their low densities, because they have been or are utilized for density measurements of plutonium and uranium, respectively, and their cost is quite low.

Mallett⁽⁶⁾ has reported experimental work with 1-octanol. He found agreement with the theoretical temperature-density curve plotted from the data of Dreisbach and Martin⁽²¹⁾ within ± 0.1 g/cc. He also found a minimal weight loss of 1.5 mg when uranium was immersed in 1-octanol, which was concluded to have occurred during an initial slight chemical reaction. An accuracy for nine uranium samples of ± 0.003 g/cc was found and, if a fresh surface was used, an accuracy of ± 0.009 g/cc. The optimum accuracy under the conditions of measurement was determined as being ± 0.001 g/cc.

Possibilities from the Beryllium Group

One common factor that is true of all the solvents in Table II, except 1-octanol and monobromobenzene, is that the densities are greater than any of those considered for beryllium. This was an arbitrary decision, however, and there is the possibility that a given solvent in the beryllium group would be as much or more suitable than any found in Table II, apart from the magnitude of its density.

(6) loc. cit., p 4

(21) Dreisbach, R. R., and Martin, R. A., Industrial and Engineering Chemistry, 41, 2875-78 (1949).

Three solvents from Table I that might be possibilities for uranium and plutonium are 1-bromo, 2-chloropropane, 2-bromoethanol, and 1-bromo-4-fluorobenzene. The first two should be equivalent to the bromopropanes in radiation stability and the last compound should rank ahead of 1-octanol and monobromobenzene in radiation stability. The 1-bromo-4-fluorobenzene has the disadvantage of high cost.

"Freon-113" has high radiation stability, but its high evaporation rate makes its usage in a glovebox or hood, where there is a rapid air flow, somewhat dubious.

R E C O M M E N D A T I O N S

BERYLLIUM

"Freon-113" 1,1,2-Trichlorotrifluoroethane

"Freon-113" is a very strong first choice for the following reasons:

- 1 Purity
- 2 Very low toxicity
- 3 Nonflammability
- 4 Low surface tension
- 5 Chemical stability
- 6 Good precision relevant to its temperature-density curve
- 7 Lack of objectionable odor.

Chief disadvantages are:

- 1 Low heat capacity
- 2 Relatively high rate of evaporation.

Nevertheless, because of its successful use with beryllium at Rocky Flats, "Freon-113" was given strong consideration for use as a density immersion medium for both plutonium and uranium at Rocky Flats. After further comparative testing with monobromobenzene and the design of proper facilities, "Freon-113" was put into use for density measurements of plutonium in August, 1965.

A comparison of the corrosive properties of "Freon-113" and monobromobenzene by the Basic Chemistry Group showed that the corrosive effects of monobromobenzene are more than twice as great as for "Freon-113". A closer comparison of the reproducibility of measurement showed that "Freon-113" is much superior.

One potential problem was the fact that "Freon-113" exerts a cleaning action on the metal which tends to leave a residual material in the liquid. The density of this material was found to be such, however, that it quickly settles out. By contrast, it was found that the residual material produced by the cleaning action of monobromobenzene does not settle out due to its colloidal nature and contributes significantly to erratic density measurements. In fact, the variability in density was found to be such as to almost exceed the limits set by the design specifications. Utilizing "Freon-113", the densities may be measured within a range of 0.4 mg/cc with a reproducibility of ± 0.02 mg/cc.

Another potential problem was the cooling action of "Freon-113" on metal samples as they are immersed due to its low heat capacity. It was found that temperature equilibrium is achieved quite rapidly, however, and so this is not a serious problem.

To minimize evaporation losses, the air flow was reduced in the density-measuring glovebox and covers placed on the liquid storage compartments. The amount of evaporation is still large enough to make the monthly cost of solvent a significant item.

On the basis of available information, there are no technical objections to the usage of "Freon-113" and its employment as a density immersion medium for beryllium is to be highly recommended. Minimal venting requirements mean that a substantial reduction in the cost of required operating facilities may be achieved. The low heat capacity and relatively high evaporation rate of this solvent need not pose as serious problems, if handled appropriately.

Secondary Choices

- 1 2-bromoethanol
- 2 1-bromo,2-chloroethane
- 3 1,2-dibromo,2-methylpropane
- 4 1-bromo,4-fluorobenzene

The reasons for these choices have been cited earlier based on the information provided in Table I. Were it not for cost, the number four choice would rank higher.

URANIUM AND PLUTONIUM

Ethene Compounds

Exclusive of cost, 1,1,2-tribromoethene and 1,2-dibromoethene are the best choices for the following reasons:

- 1 Postulated radiation stability
- 2 Chemical stability
- 3 Relatively high density
- 4 Relatively low toxicity.

If costs were prohibitive, other choices would prevail. It is to be noted, however, that if an expensive compound has a significantly lower evaporation rate and a significantly higher radiation stability, the extra cost may be commensurate with the overall cost of a cheaper, but more volatile and less radiation stable, compound.

Other Choices

- 1 (a) 1,1,2-tribromoethane
(b) 1-octanol
- 2 (a) 1,3-dibromopropane
(b) 1,2,3-tribromopropane
(c) 1,2-dibromopropane
- 3 "Freon-113"
- 4 Monobromobenzene.

The 1-octanol compound seems quite desirable for uranium, at least, as discussed earlier. Its seemingly chief disadvantage is its very low density. The 1,1,2-tribromoethane is moderately toxic and has only a moderate radiation stability.

The third choices are the bromopropane compounds, whose cost varies considerably between members but whose most costly member should have the greatest radiation stability.

On the basis of present experience at Rocky Flats, "Freon-113" must rank as at least the fourth choice. Its purity, lack of toxicity, chemical stability, and reproducibility of measurement make it superior to monobromobenzene, despite its high cost. Monobromobenzene is the fifth choice on the basis of its reasonably successful use at Rocky Flats for plutonium and uranium density measurements. The fact that the liquid density of this solvent does undergo significant changes due to accumulation of residual material and that these variations are only just within the design specification limits, plus its disagreeable handling characteristics, make it a somewhat dubious choice.

Further Experimental Work

In conclusion, there are enough unknown variables to merit experimental work with several chemical compounds to ascertain their suitability for the intended density measurements with uranium and plutonium. Such properties as vapor pressure, chemical inertness, radiation stability, toxicity, purity, specific heat, and flammability should be determined where unknown. Once the more important of these properties have been ascertained, the temperature-density curves of the more-promising compounds could be determined.