

measurements, might have been caused either by a continued liberation of air occluded in the sample or by the steady production of a volatile decomposition product in small amount (that a slight decomposition did occur was indicated by a gradual darkening of the sample). This explanation gains in plausibility from the fact that the measured vapor pressures for two of the plastics exceed somewhat the vapor pressure of the pure plasticizer.

TABLE VI

VAPOR PRESSURES OF POLYVINYL CHLORIDE-TRI-*m*-CRESYL PHOSPHATE PLASTICS

% polyvinyl chloride..... ^a	0 ^a	40	40	70	85
114	1.44	1.38	1.68	1.37	1.79
119	2.29				3.17
124	3.59		4.19		4.17
129	5.57		6.02	4.97	7.02

^a Calculated values (cf. Table V).

It seems reasonable to conclude that the vapor pressure of the plasticizer in these plastics is independent of concentration over the range 15–100% plasticizer. More results will be needed with other plasticizers to confirm this conclusion. It is possible that the quantity being measured in these experiments is the vapor pressure of a film

of plasticizer on the surface of the plastics. Since the slope of the vapor pressure curve and also its absolute position is the same for the plastics and the pure plasticizer, it may be concluded from this type of experimentation that the heat involved on mixing polyvinyl chloride and tricresyl phosphate is practically zero. To confirm this conclusion it would be desirable to carry out calorimetric experiments on the heat of wetting at elevated temperatures of polyvinyl chloride by several plasticizers.

Summary

The vapor pressures of tri-*m*-cresyl phosphate, tri-*p*-cresyl phosphate, dibutyl phthalate and dibenzyl sebacate in the neighborhood of 100° have been measured by a static and by dynamic methods.

The accommodation coefficients for these liquids are unity.

The vapor pressure of the plasticizer in a polyvinyl chloride-tri-*m*-cresyl phosphate plastic containing at least 15% of the latter appears to be equal to the vapor pressure of the pure plasticizer and is independent of the composition of the plastic.

SCHENECTADY, N. Y.

RECEIVED JUNE 21, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MISSOURI, AND THE NEW MEXICO NORMAL UNIVERSITY]

Pied des Monts Uraninite

BY O. B. MUENCH

A fine specimen of uraninite was collected from the Lac Pied des Monts district in Quebec and given to Mr. H. S. Spence,¹ who sent it by way of Dr. A. C. Lane² to the writer for an age determination by the lead-uranium method and for the extraction and preservation of the lead for an isotopic determination to be made later by A. O. Nier at Harvard University. This material is of interest since considerable work has been done by Ellsworth³ on samples from this district. He gives a description of the geological occurrence of minerals in this district, accompanied by a complete chemical analysis and age determination.

(1) Mining Engineer, Mines Branch, Department of Mines, Canada.

(2) Chairman of the "Committee on the Measurement of Geologic Time."

(3) Report of the Committee on the Measurement of Geologic Time, 1934: *Am. Min.*, **19**, 421–425 (1934).

Another interesting account of the location, with references, is given in *Le Naturaliste Canadien*.⁴ Material from this location has been called cleveite⁵ by some, but Ellsworth,³ Berman,⁶ and others prefer the term uraninite for this mineral.

The surface of the mineral did not show any indication or sign of secondary uranium minerals. Before beginning the analysis, several autoradiographs were made of various pieces of the specimen on different smoothly ground surfaces. Some sections were cut through the middle and autoradiographs made of these. The prints seem to in-

(4) Carl Faessler, "La Cote Nord," *Le Naturaliste Canadien*, April, 1932, pp. 100–102.

(5) *J. Can. Min. Inst.*, **7**, 245–256 (1904). Obalski first mentioned the location and found the large crystal from which Ellsworth determined the lead ratio on a small sample.

(6) Dr. Berman of the Harvard Department of Mineralogy in a private communication to Professor A. C. Lane.

dicates a fairly uniform distribution of radioactive material and no visible evidence of leaching.

figures, and using the logarithmic formula of Holmes,⁹ is

$$\text{Analysis} \quad \frac{\log (U + 0.36\text{Th} + 1.155\text{Pb}) - \log (U + 0.36\text{Th})}{6.6 \times 10^{-5}} \text{ million years} = 956 \text{ million years.}$$

The sample was broken into smaller pieces in a clean iron mortar and then finely powdered in a clean agate mortar to pass a 100-mesh sieve. The precautions necessary to this type of analysis were observed carefully to avoid contamination. Special precautions were taken in this respect with the lead. Pure analytical reagents were used, and these were purified further where the accuracy of the analysis depended upon it.

The lead sulfate from the lead determination was saved and sent to Alfred O. Nier at Harvard University for the isotopic determination. His analysis¹⁰ has direct reference to this paper, and is of special interest in this age determination since it gives the figures for the isotopic composition of the lead which was used in this determination. The following is from his paper, with 206 taken as 100 in the proportion of isotopes

The sample was decomposed in nitric acid and the silica removed in the usual way. The lead, after separation and purification, was weighed as the sulfate. Recoveries for lead were made on all filtrates and from the silica.

Pb	204	206	207	208
	0.047 = 5%	100	7.60	1.92 = 2%
	Mass number		Physical atomic weight	
	206.103		206.078	
	= 0.002			
Ac D/Ra G		Pb/U		Ra G/U ²³⁸
%				
6.88		0.1354		0.1233

The uranium was determined as the pyrophosphate,⁷ which method is described in detail in previous papers.

Age, accordingly in million years: 903 by Ac D/Ra G
882 by Ra G/U²³⁸

Four five-gram samples were run for thorium by the iodate method, which also is described in previous papers.^{7,8} The very small, hardly weighable residue carried some of the rare earths in the form of oxides as indicated by the pale yellow color.

Calculation from the lead-uranium ratio without taking into consideration the isotopic composition of the lead yields an age of 956 million years.

TABLE I
RESULTS

Lead		
Sample, g.	PbSO ₄ , g.	Lead, %
1.0005	0.0975	6.655
1.0024	.0979	6.675
1.0016	.0981	6.689
1.0020	.0978	6.666
1.0000	.0976	6.666
	Average	6.670

Uranium		
Sample, g.	(UO ₂) ₂ P ₂ O ₇ , g.	Uranium, %
0.2025	0.1495	49.22
.2016	.1488	49.23
.2027	.1498	49.29
.2013	.1487	49.27
	Average	49.25

Thorium

Four separate five gram samples quantitatively gave only a slight indication of thorium. Rare earths were present. 0.0% Thorium.

Loss on ignition..... 12.07%
Loss at 100° for four hours..... 0.41%

The lead-uranium ratio is 6.67/49.25 = 0.135.

The results of Nier's isotopic analysis of the lead from this sample indicate that about 4% of the lead is common lead. Correcting the lead percentage for this amount of common lead, changes the lead figure from 6.67 to 6.40%. This correction alters the lead-uranium ratio to 0.130. The corresponding age calculated by the logarithmic formula is 920 million years, which is nearer to Nier's ages determined by different methods.

Nier in his paper¹⁰ has pointed out the fact that uranium rather than lead is usually lost whenever alteration takes place in a uranium mineral, thus making the lead-uranium ratio too high, whereas the age computed from Pb²⁰⁷/Pb²⁰⁶ ratio hardly differs from the true age of the mineral.

The age of this mineral, calculated from the above

Acknowledgments.—The author is indebted to the Geological Society of America for financial assistance in part, for this work; to Professor A. C. Lane for his constant inspiration and encouragement; to Mr. H. S. Spence for the mineral; and to the late Dr. Herman Schlundt and the University of Missouri for the generous use of laboratories, chemicals, and other facilities.

(7) Muench, THIS JOURNAL, 59, 2269 (1937).

(8) Method of Meyer and Speter as given by Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, p. 420.

(9) A. Holmes, National Research Council, Washington, Bull. 80, 207 (1931).

(10) A. O. Nier, Phys. Rev., 55, 158-159 (1939).

Summary

The lead-uranium ratio of a uraninite from Lac Pied des Monts, Quebec, was determined as 0.135. The analytical results show 6.67% lead, 49.25% uranium, and a trace of thorium.

An isotopic determination on the lead obtained from this analysis was made by A. O. Nier at Harvard University. With these results available, the age of the Lac Pied des Monts uraninite can now be given with greater assurance and accuracy. Corrections for common lead made

from Nier's determination change the percentage to 6.40 and the lead-uranium ratio to 0.130. The age of the mineral, calculated with these corrected figures, is 920 million years and compares favorably with the results calculated from the isotopic determination of the lead from this sample.

Two independent age determinations made by entirely different methods on the same specimen yield results in fairly good agreement.

LAS VEGAS, N. M.

RECEIVED MAY 22, 1939

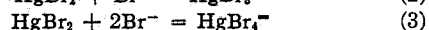
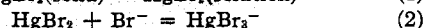
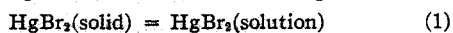
[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Solubility of Mercuric Halides in Solutions of Potassium Halides. The Character of the Mercuric Halide Complex Ions. Evidence for Polymerization of Mercuric Chloride

BY A. B. GARRETT

The purpose of this paper is to present measurements of the solubility of mercuric halides in halide solutions and to calculate the equilibrium constants for the reactions involved in the formation of the complex mercuric halide ions; the values of these constants should indicate the character of the complex ions of mercury in the solutions studied.

The moderately low solubility of mercuric bromide and mercuric iodide makes possible a fairly direct determination of the character of the complex ions of these mercuric halides by means of solubility measurements. Additional information essential to this determination are these facts: (1) earlier work¹⁻⁶ has shown that the mercury halides are only slightly dissociated and (2) their solubility in halide solutions is predominantly specific to the concentration of the halide ion and not to the ionic strength. These facts make it possible to attribute the solubility of mercuric halides in halide solutions mainly to several or to all of the following reactions (using the bromide as an example)⁷



(1) Thomas, *THIS JOURNAL*, **61**, 920 (1939). This paper contains a very good bibliography on the mercuric chloride-chloride system.

(2) Herz and Paul, *Z. anorg. Chem.*, **82**, 431 (1913).

(3) Abegg (with Immerwahr and Jander), *Z. Elektrochem.*, **8**, 689 (1902); (with Sherrill) **9**, 550 (1903).

(4) Sherrill, *Z. physik. Chem.*, **43**, 727 (1903).

(5) Le Blanc and Noyes, *ibid.*, **6**, 389 (1890).

(6) Richards and Archibald, *ibid.*, **40**, 385 (1902).

(7) See latter section of this paper for additional equilibria that may exist in the $\text{HgCl}_2\text{-Cl}$ system.

The data necessary are those in low concentrations where one might reliably expect the limiting law to be applicable. Only a meager amount of such data is available from early work.¹⁻⁶

Early work is at variance with respect to definite conclusions concerning the character of these halide ions. A number of workers^{3,8-10} have claimed the formation HgCl_3^- , HgBr_3^- or HgI_3^- whereas others¹¹⁻¹³ submit evidence for the HgI_4^{2-} ion. Job¹¹ claims the presence of KHgCl_3 , $\text{K}_2\text{-HgBr}_4$ and K_2HgI_4 in their respective solutions. Sherrill⁴ even gives data on the ionization constants for all of these salts, *i. e.*, KHgI_3 , K_2HgI_4 , KHgBr_3 , K_2HgBr_4 , etc. Tananaev and Piliipenko¹³ assumed the near 2 to 1 ratio of added potassium iodide to mercuric iodide indicated the formation of HgI_4^{2-} predominantly.

Procedure.—Baker c. p. quality and Mallinckrodt Analytical Reagent mercuric bromide and mercuric iodide were used. For a number of preparations the mercuric bromide was recrystallized from hydrobromic acid solution and heated at 115° for four hours to assure complete removal of any hydrogen bromide. The same procedure was followed with the mercuric iodide but the recrystallization was omitted.

Baker Analytical Reagent potassium bromide and potassium iodide were used.

(8) Naude, *Z. physik. Chem.*, **125**, 98 (1927).

(9) Pernot, *Compt. rend.*, **185**, 950 (1927); *Ann. chim.*, [10] **15**, 5 (1931).

(10) Dunningham, *Proc. Chem. Soc.*, **30**, 8 (1914); *J. Chem. Soc.*, **105**, 368 (1914).

(11) Job, *Ann. chim.*, **9**, 113 (1928), from light absorption studies.

(12) Golse, *Compt. rend.*, **190**, 873 (1930), from studies on the equilibrium $\text{AgNO}_3 + \text{HgI}_2 + \text{KI}$.

(13) Tananaev and Piliipenko, *J. Applied Chem. (U. S. S. R.)*, **10**, 549 (1937).