American Mineralogist, Volume 58, pages 1084–1087, 1973

New Diluents in Heavy Liquid Mineral Separation and an Improved Method for the Recovery of the Liquids from the Washings

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Abstract

Isoamylacetate and orthodichlorobenzene have been tested and are recommended as diluents for bromoform and diiodomethane, respectively. As washing liquid for these solutions 1.1.1. trichloroethane is recommended. Procedures for the preparation and calibration of the heavy liquid solutions are described. An efficient method has been developed for the recovery of heavy liquids and washing liquid, employing a rotary film vacuum evaporator.

Introduction

Heavy liquid solutions based upon bromoform and diiodomethane are widely used in mineral separation. When employing bromoform solutions, the commonly used diluents are ethyl alcohol, carbon tetrachloride and benzene (Krumbein and Pettijohn, 1938, p. 321), dimethylsulfoxide (Meyrowitz, Cuttitta, and Levin, 1960), N,N-dimethylformamide (Hickling, Cuttitta, and Meyrowitz, 1961), and decaline (Doeglas, Favejee, Nota, and Van der Plas, 1965). Liquids advocated as diluents for diiodomethane are di-n-butylphtalate (Muller and Burton, 1965) and N,N-dimethylformamide (Meyrowitz *et al,* 1960).

Bromoform and diiodomethane, when chemically pure, have specific gravities of 2.88 and 3.31, respectively. Since both liquids decompose and darken on standing, they have to be stabilized. For bromoform this stabilization is usually achieved by addition of 1 percent of its weight of ethyl alcohol, while decomposition of diiodomethane is prevented by addition of some metallic silver. However, the big difference in vapor pressure between bromoform and ethyl alcohol (Table 1) makes bromoform stabilized with ethyl alcohol unsuitable for the preparation of solutions that have to be constant in specific gravity. Therefore, ethyl alcohol has to be removed (extraction with water and drying with calcium chloride) until the bromoform has a specific gravity of 2.876 at 25°C, which is an adequate criterion for the purity of the liquid; addition of some other stabilizer is then required.

N,N-dimethylformamide has been especially recommended as a diluent for both bromoform (Hickling *et al,* 1961), and diiodomethane (Meyrowitz *et al,* 1960). Its physical properties are included in Table 1. These solutions maintain relatively constant specific gravities during use and in storage, but are not wholly stable and decompose during use and/or long standing. Hickling *et al* (1961) reported a slight darkening in the color of bromoform-dimethylformamide solutions after use, while Meyrowitz *et al* (1960) noticed that diiodomethane-dimethylformamide mixtures become red when not stored in contact with metallic copper.

New diluents

Two liquids have been tested and are recommended as diluents for the preparation of heavy liquid solutions, *i.e.,* isoamylacetate for bromoform and orthodichlorobenzene for diiodomethane. The salient physical properties of the liquids are summarized in Table 1.

When employing heavy liquid solutions based upon bromoform, isoamylacetate has advantages as a diluent above the other liquids previously mentioned: (1) its vapor pressure is very close to that of bromoform (Table 1), and (2) it has proved to be an excellent stabilizer for bromoform. Solutions of isoamylacetate and pure bromoform are therefore very constant in specific gravity and do not decompose during use or in storage. The minimum amount of isoamylacetate that has to be added in order to stabilize bromoform is about 1 percent of its weight, resulting in a liquid with a specific gravity of 2.82. It is thus possible to obtain stable and constant solutions over the density range 2.82 to 0.87 (g/ml) at 25°C.

The orthodichlorobenzene proposed here has been

found to be a more suitable diluent for diiodomethane than di-n-butylphtalate or N,N-dimethylformamide. Due to the closely similar vapor pressures (Table 1), diiodomethane-orthodichlorobenzene solutions remain very constant in specific gravity. Moreover, these solutions do not decompose during use or, if proper care is taken to store the liquids in dark bottles in a refrigerator, on long standing. Orthodichlorobenzene acts as a good stabilizer in the solutions, but pure diiodomethane has always to be kept in contact with some metallic silver.

In order to test the constancy in specific gravity of bromoform-isoamylacetate and diiodomethane-orthodichlorobenzene solutions during use, a series of solutions was prepared. Each liquid was then rotated for one hour in the laboratory overflow-centrifuge described by IJlst (1973). For comparison, the same procedure was applied to bromoform-dimethylformamide and diiodomethane-dimethylformamide solutions. The specific gravities of the solutions before and after the rotation are given in Table 2. From these data it is evident that there is a very good constancy of the mixtures with isoamylacetate and orthodichlorobenzene, even slightly better than observed for the corresponding solutions of bromoform and diiodomethane with N,N-dimethylformamide in the specific gravity range mostly used for mineral separation.

After two years in storage, the bromoform-isoamylacetate and diiodomethane-orthodichlorobenzene solutions did not show any decomposition or measurable change in specific gravity.

No problems exist involving the toxicities of the diluents proposed here. The threshold limit values of orthodichlorobenzene and isoamylacetate are 50 ppm and above 100 ppm, respectively, versus 0.5 ppm for bromoform (Riddick and Bunger, 1970).

Preparation and calibration of the solutions

Solutions of the desired specific gravity may be prepared by weighing the end members. This is preferred above the commonly applied method of mixing calibrated volumes of heavy liquid and diluent (for example, Woo, 1964; Muller and Burton, 1965), because precise measurement of small amounts of liquids is somewhat easier by weight than by volume. The following formula is used to arrive at the desired specific gravity:

$$m_l = m_h \cdot \frac{(d_h - d_d) \cdot d_l}{(d_d - d_l) \cdot d_h}$$

TABLE 1. Physical Properties of the Liquids Used*

	Melting point °C	Boiling point °C	Specific gravity d_4^{25}	Vapor pressure in torr 20°C	25°C	30°C	Viscosity 25°C cp
			Heavy Liquids				
bromoform	8.0	149.5	2.8758	4.6	5.9	7.9	1.89
diiodomethane	5.6-6.1	182 *d*	3.3078	0.9	1.2	1.7	2.07
			Diluents				
isoamylacetate	-78.5	142.0	0.8664	4.5	5.5	7.3	0.80
orthodichlorobenzene	-17.0	180.5	1.3003	1.0	1.3	1.9	2.41
dimethylformamide	-60.0	155.0	0.9440	2.7	3.7	5.1	0.80
ethyl alcohol	-114.1	78.3	0.7850		59.8		1.08
			Washing Liquid				
1.1.1.trichloroethane	-30.4	74.0	1.3293		120.7		0.80

* Riddick and Bunger, 1970.

where

m_l = mass of the portion of the light end member,
m_h = mass of the portion of the heavy end member or solution,
d_h = specific gravity of the heavy end member or solution,
d_l = specific gravity of the light end member,
d_d = desired specific gravity of the mixture.

Heavy liquid and diluent have to be carefully mixed. However, due to different molecular attractions in the liquids, the bromoform-isoamylacetate and diiodomethane-orthodichlorobenzene mixtures have a somewhat greater volume than that from the arithmetical addition of the volumes of both end members. This has to be taken into account when preparing a solution of desired specific gravity d_d, so the above formula is not strictly valid.

For solutions of bromoform and isoamylacetate in the specific gravity range between 2.50 and 2.80, the difference between d_d prepared according to the above formula and the measured value is always less than 0.001. For all practical purposes, this deviation can be neglected. The specific gravities observed for diiodomethane-orthodichlorobenzene mixtures, on the other hand, do deviate much more from the set value d_d. In order to correct for this deviation, d_d in the above formula has therefore to

TABLE 2. Changes in Specific Gravity after One Hour's Rotation in the Overflow-Centrifuge

	Specific gravity* before use d_4^{25}	after use d_4^{25}	Change
bromoform-isoamylacetate	2.6429	2.6399	-0.0030
bromoform-dimethylformamide	2.6442	2.6343	-0.0099
diiodomethane-orthodichlorobenzene	3.1326	3.1426	+0.0100
diiodomethane-dimethylformamide	3.1238	3.1384	+0.0146

*Precision ± 0.0002 (3σ).

be replaced by d_d^*, where

$$d_d^* = d_d + (\delta_h - \delta_d).$$

The δ values were empirically determined for diiodomethane-orthodichlorobenzene solutions in the specific gravity range from 2.80 to 3.25 and are listed in Table 3.

In mixtures of diiodomethane and N,N-dimethylformamide, the combined volumes of both end members are likewise somewhat greater than their arithmetical addition. Therefore, contrary to the statement by Meyrowitz *et al* (1960), a simple straight-line mixing curve (volume + volume) cannot be used to prepare a liquid of desired specific gravity with some accuracy.

The specific gravity of the solution is determined with the aid of an electrical balance equipped as a Westphal balance. Using a glass sinker with a mass of 54 g and a volume of 10 ml, it is possible, employing a balance with a precision of ± 1 mg, to obtain a precision of ± 0.0002 (3σ) for the determination of the specific gravity of the solution. The whole determination is carried out in a double-walled glass beaker with thermostatically controlled water circulating between the walls.

Determination of the specific gravity of the solution can also be based upon the measurement of its refractive index by means of an Abbe refractometer. Both the liquid and the refractometer have to be held at a thermostatically controlled temperature during the measurement. However, this method is less sensitive: the precision in the specific gravity determined in this way is ± 0.006 (3σ). Mixtures of bromoform and isoamylacetate show a linear correlation between the specific gravity and the refractive index in the range from pure bromoform with $d_4^{25} = 2.8758$ ($n_D^{25} = 1.5945$) to a solution with $d_4^{25} = 2.5000$ ($n_D^{25} = 1.5563$). No linear correlation exists for mixtures of diiodomethane and orthodichlorobenzene; the observed correlation is shown in Figure 1.

The thermal coefficient of the specific gravity has been determined at 0.0027/°C for bromoform and bromoform-isoamylacetate solutions down to a specific gravity of 2.50. For diiodomethane and mixtures of diiodomethane and orthodichlorobenzene with specific gravities down to 2.80, the same value has been measured.

TABLE 3. Values of δ Determined for Mixtures of Diiodomethane and Orthodichlorobenzene

Specific gravity	δ value	Specific gravity	δ value	Specific gravity	δ value
3.25	0.0031	3.10	0.0097	2.90	0.0157
3.20	0.0056	3.00	0.0130	2.80	0.0178

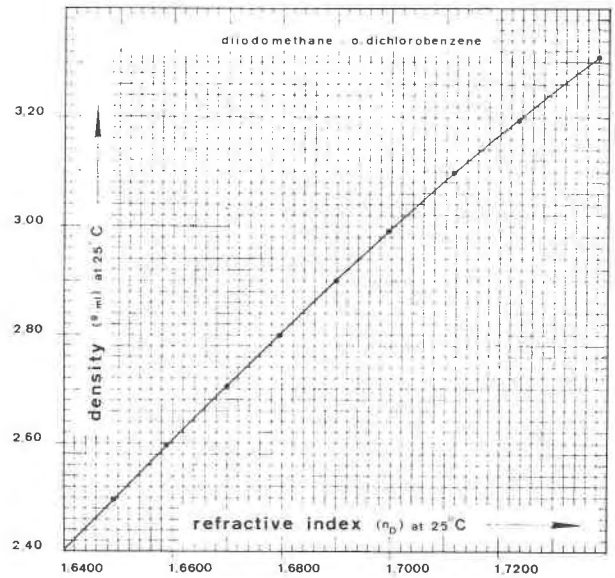

FIG. 1. Correlation between specific gravity and refractive index for mixtures of diiodomethane and orthodichlorobenzene (at 25°C).

Washing liquid and recovery of the liquids

Use of a washing liquid is essential for the recovery of a heavy liquid solution after the mineral separation. The commonly used liquids for this purpose are ethyl alcohol, benzol, acetone, and trichloroethylene. For health and safety reasons, 1.1.1.trichloroethane is preferred by the author as a washing liquid above these commonly used liquids (threshold limit value 350 ppm; *cf* Riddick and Bunger, 1970). The salient physical properties of this liquid are given in Table 1.

Recovery of bromoform and diiodomethane from the 1.1.1.trichloroethane washings is obtained by distillation in a standard rotary film "vacuum" evaporator with the evaporator flask rotating in a water bath held at about 90°C. In the distillation system, a diminished pressure of 400 torr is maintained by means of a water pump. Under this reduced pressure the boiling point of 1.1.1.trichloroethane is approximately 55°C. The evaporator flask has a content of 1000 ml and rotates with 100 rpm.

Due to the moderate temperature and the relatively short time required for the distillation (1000 ml of the mixture of heavy liquid and 1.1.1.trichloroethane can be processed in about 30 minutes), bromoform and diiodomethane are very little affected by decomposition during the distillation. This is an important advantage above the various types of "open distillation" commonly used. The residual heavy liquid in the evaporator flask is further purified from the remaining washing liquid by freezing and shaking with activated carbon (Norite Rwx 1). The purification of the 1.1.1.trichloroethane collected in the receiver flask is carried out with a conventional fractional distillation process. Losses of heavy liquids and of washing liquid are minimized with these procedures.

Acknowledgments

The author benefited much from critical discussions with Dr. R. H. Verschure, Professor H. N. A. Priem, and Dr. E. H. Hebeda. He thanks Professor Priem for his help in preparing the manuscript of this paper. This work forms part of the research program of the "Stichting voor Isotopen-Geologisch Onderzoek," supported by the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

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Manuscript received, May 18, 1973; accepted for publication, July 18, 1973.