RECOVERY OF HEAVY LIQUIDS
FROM DILUTE SOLUTIONS

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Abstract

Semi-automatic methods for the recovery of organic and inorganic heavy liquids are described. The method for solutions of inorganic salts, *e.g.* Clerici's solution, depends upon the variation of boiling point with salt concentration, and utilises a temperature sensor to halt evaporation at the desired density. For organic liquids, a semi-automatic washing apparatus for the removal of water-soluble diluents is described, constructed of readily available parts. The losses with various diluents at varying washing times are detailed, and compared to simple washing with large volumes of water. Using the apparatus described, losses as low as $<2\%$ are obtained, as opposed to a commonly accepted 10%.

Heavy liquids are a basic tool of every mineralogical laboratory, and their routine use produces large volumes of diluted liquid as a result of washing separated materials and from density-gradient use. Because of the high cost of the pure liquids, these solutions cannot be discarded and attempts are invariably made to recover the original heavy liquid.

High-density liquids commonly used can be divided into two groups for the purposes of this paper:

(1) Organic-including methylene iodide, bromoform, and tetrabromo-ethane,

(2) Inorganic-aqueous solutions of heavy-metal salts.

Diluents used for these liquids include water, acetone, tri-ethyl orthophosphate, and NN-dimethyl formamide. Table 1 summarizes the physical properties of some of the more generally used liquids.

Methods for the recovery of the original heavy liquid obviously vary with the nature of the liquid and diluent. Common methods are: (1) Evaporation-used only with aqueous solutions, (2) Freezing-used with nonwater soluble diluents, (3) Washing with water-used with water-soluble diluents.

In many laboratories, recovery is carried out in a haphazard fashion, washings being accumulated until they occupy too large a volume, then some variant of the above procedure is carried out. These methods are often very wasteful of the heavy liquid, because of spillage, evaporation, etc. (*cf.* Muller and Burton, 1965, p. 1157, where 10 percent losses are accepted.) This paper suggests methods of recovery that minimize such losses.

Inorganic (Aqueous) Solutions

For such liquids, evaporation of water by boiling is the common, and only practical, means of reconcentration. This is often attended by dif-

TABLE 1. PHYSICAL PROPERTIES

Liquid	Formula	Density g/ml at 20°C	Refractive Index ng at 20°C	Viscosity cP at 20°C	Vapour Pressure τ at 20°C	Solubility in g/100 ml water at 20°C
Bromoform	$CHBr_3$	2.8899	1.5976	2.152^{15} 1.89^{25}	5	0.319
Tetrabromo-ethane	$CHBr_2 \cdot CHBr_2$	2.9672	1.6380	12.0	<1	0.065
Methylene iodide	CH_2I_2	3.325	1.7407	2.6	1.25^{25}	1.42
Clerici's solution	$CH_2(COOTl)_2 \cdot$ $H \cdot COOTl$	4.28^a	1.705	31.0	—	1400–2000
Acetone	$CH_3 \cdot CO \cdot CH_3$	0.792	1.5387	0.32	285	∞
NN-dimethyl formamide	$HCON(CH_3)_2$	0.93445^{25}	1.42669^{25}	0.80^{25}	2.7	∞
Tri-ethyl phosphate	$(C_2H_5)_3PO_4$	1.0686	—	—	<1	100 (d)
2-methoxy ethyl acetate	$CH_3 \cdot COOCH_2 \cdot CH_2OCH_3$	1.0090	—	—	—	∞

15 = measured at 15°C.

25 = measured at 25°C.

(d) = with decomposition.

^{a} = can attain >4.85 g/ml at 80°C.

Source: Handbook of Chemistry & Physics, 46th Edition, 1956–66, Chemical Rubber Publishing Co., Ohio.

ficulties, *e.g.*, unless continuously monitored, evaporation is often carried too far, even to the point of complete dryness, resulting in the destruction of the salts involved. A completely automatic method which results in a liquid of the desired density, is desirable and easily evolved. The apparatus described utilizes the variation in boiling points of solutions with different salt concentrations (and thus density). It consists essentially of a heating element controlled by a sensitive temperature regulator. The sensing element is an encapsulated thermistor immersed in the liquid in a flask. This unit can perform two functions: (1) With the addition of a cut-out relay in the circuit, it will switch itself off when any desired temperature has been attained in the solution; (2) without the relay, it will function as a sensitive thermostatic unit.

The unit was constructed using the following:

A.E.I. "Sunvette" thermostatic control unit, supplied with a thermistor for use within the range 0–130°C. Any transistorised control circuit, such as can be found in most electronic handbooks, will serve equally well.

A cut-out relay (simply constructed by any instrument laboratory).

An electric heating mantle to accommodate 1- or 2-liter flasks, whichever is most suited to the volume of washings to be treated.

A probe-housing for the thermistor. A 5 mm glass tube, heat-sealed at one end, and filled with a non-polar high boiling-point liquid, such as Esso heat-transfer oil, will serve. The liquid is necessary both as insulation for the wiring (because normal plastic sleeves melt at about 100°C) and as a heat conductor to the thermistor.

Each circuit will have its own characteristics, as will the heavy liquid solutions made up by different investigators; both must, therefore, initially be calibrated. As a guide to such variation, data from the prototype unit is given in Figure 1.

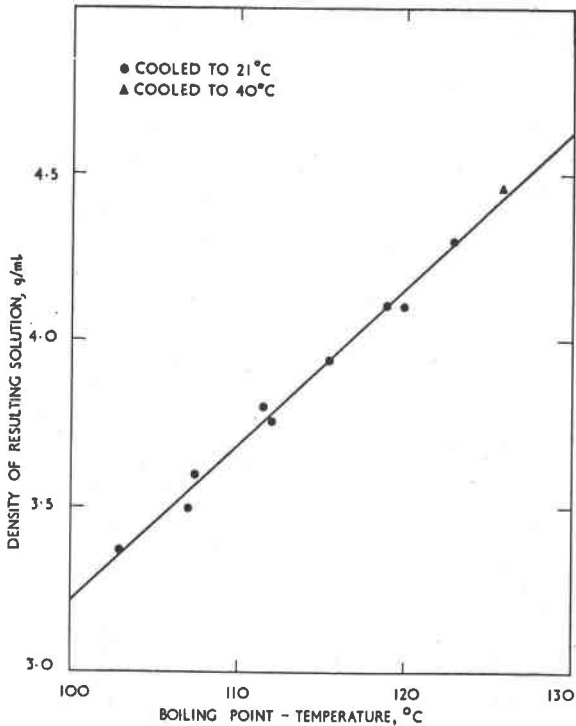The unit requires no supervision in use, and is fairly rapid in action—a liter of very

FIG. 1. Variation of density (measured at indicated temperature) of
an aqueous heavy liquid with boiling point.

dilute washings can be brought to a density of 4.3 g/ml in about 30 minutes. There is no
danger of over-evaporation, because shutdown is automatic. In comparison with the cost
of the heavy liquid, the unit is cheap and simple to construct.

Organic Heavy Liquids

The only easy and cheap method of recovery of such liquids is washing
with water. For this to be effective, the diluents should have low vapor
pressure, approximating that of the heavy-liquid (to give stable diluted
solutions), low viscosity, low cost, and infinite solubility in water at room
temperatures. Of a large number of possibilities, NN-dimethyl formamide
(Hickling, et al., 1961; Meyerowitz, et al., 1960) appears to be the most
satisfactory. A basic disadvantage of the method is that all the com-
monly-used heavy liquids are, to a certain extent, soluble in water (see
Table 1). In addition to being the most expensive, methylene iodide has
the highest solubility, but for most purposes in the ore-dressing lab-
oratory, its much higher density more than compensates for these faults.

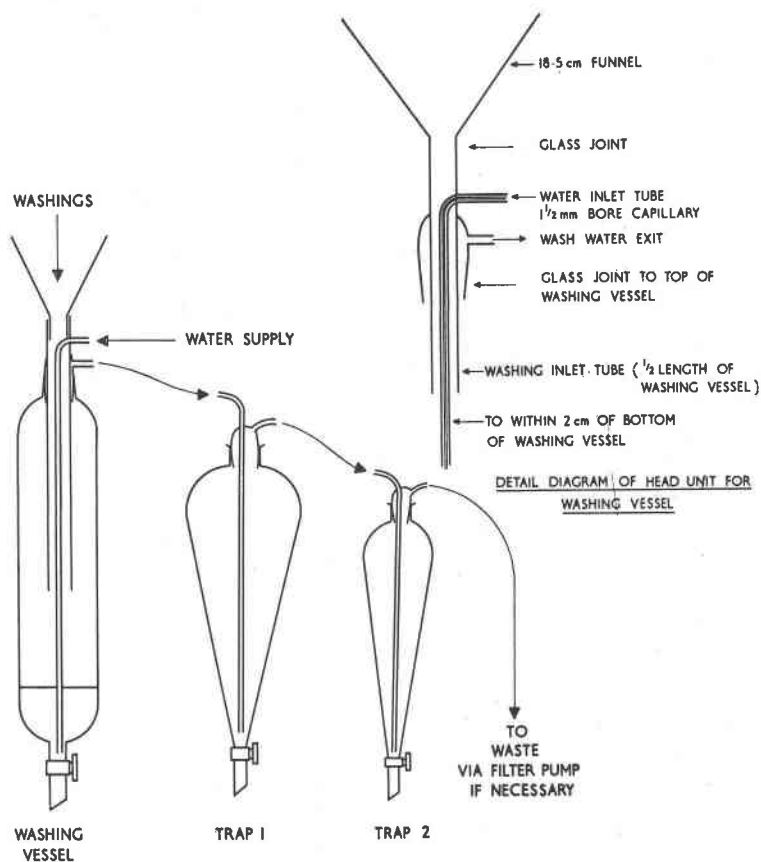The described recovery apparatus is designed to give minimum wash water volumes

FIG. 2. Schematic diagram of organic heavy liquid recovery unit;
detail diagram of head unit for washing vessel.

consistent with removal of the bulk of the diluents and to minimise losses from other causes. It can be used for any of the organic heavy liquids mentioned, although most useful for those with high solubilities in water. The apparatus consists largely of standard items: (1) Washing vessel: 2-liter cylindrical separating funnel. (2) Trap vessels: 1-liter conical separating funnels. (3) Trap heads: gas-washing jar heads.

The only non-standard item (and this can be made-up from standard items) is the washing vessel head, the construction of which is shown schematically in Figure 2. With sufficient ingenuity, a cork can be bored to accommodate all of the necessary tubing, if glassblowing facilities are not available. A water-flow meter can be inserted into the wash-water inlet line if desired.

The various vessels are arranged in cascade fashion (Figure 2), so that

TABLE 2. WASHING TESTS

Test No.	Diluent	Volume of Diluent ml	Volume of Wash-water liters	Density of liquid recovered g/ml	Percent loss in test
1	None	—	3.5	3.306	0.8
2	Acetone	100	3.5	3.298	0.5
3	Acetone	900	3.5	3.282	1.3
4	Tri-ethyl ortho-phosphate	100	3.5	3.301	2.7
5	2-methoxy ethyl acetate	100	3.5	3.286	2.1
6	NN-dimethyl formamide	100	1.75	3.230	0.9
7	NN-dimethyl formamide	100	3.5	3.289	1.1
6	NN-dimethyl formamide	100	5.25	3.295	1.9
9	NN-dimethyl formamide	100	7.0	3.293	1.9
10	NN-dimethyl formamide	100	10.5	3.299	2.7
11	NN-dimethyl formamide	100	21.0	3.295	3.3

Notes: Volume of methylene iodide initially 100 ml at 3.291 g/ml for each test; flow rate of wash water: 350 ml/min; temperature of wash water: 8–10°C.

water will siphon from one to another, and eventually to waste. (Because the siphon method requires that the funnel inlet be closed by some means to start operation, the waste-tube may be connected to a filter-pump working at low flow rates to ensure steady operation). Water-flow through the system having been stabilized, washings are added via the funnel, and washed for a given time (see Table 2). The flow of water is such that continuous intermixing of the organic and aqueous phases is ensured, but not such that large quantities of heavy liquid are carried into the trap vessels. A flow rate, with the capillary bore described, of 300–400 ml/min is adequate. At the end of this time, the recovered heavy liquid is removed from the washing vessel by the normal means, filtered, and de-watered. It is then ready for further use.

The method described by Turner (1966) appears superficially similar to that described in this paper, but in reality depends upon simple preferential partition of diluent into the water phase from the heavy-liquid phase, with no intermixing of the two phases. Prolonged contact times of

heavy liquid with water are thus required for reasonably complete removal of diluent, and losses of heavy liquids with high solubilities in water (*e.g.* methylene iodide and bromoform) are of the order of 34–44 percent (Turner, 1966, Table 1). The figure of 97 percent recovery given by Turner for his method refers only to separations using pure heavy liquid, some 90 percent of which does not require recovery. For separations with other than pure heavy liquid, *e.g.*, quartz from feldspar, using liquid of density 2.6 gm/ml, the loss of heavy liquid on recovery will be the full 44 percent. It does not, therefore, appear that the apparatus described by Turner, from considerations of time or economics, offers any appreciable advantage over traditional techniques.

To ascertain the losses involved in reconcentration using the apparatus described in this paper, methylene iodide with various diluents was washed for set times at a standard flow rate. The volume of the recovered liquid was measured in a measuring cylinder, filtered through a phase-separating filter paper (No. 1PS) to remove the bulk of the water, and its density measured on a Westphal balance. The results are shown in Table 2. The variation of final densities achieved are in part due to variation in properties of the phase-separating paper; *i.e.*, shaking with calcium chloride increased the density of the resulting liquid in Test 7 from 3.289 to 3.311 g/ml, indicating that >99.8 percent of the diluent had been removed in 10 minutes' washing. Final densities higher than that of the methylene iodide at the start are attributable to the presence of dissolved water in the batch of heavy liquid used (which had been in use in the laboratory for some time prior to these tests being performed).

TABLE 3. SHAKING TESTS

Volume of wash water liters	Density of liquid obtained g/ml	Percent loss
1	2.842	2.1
2	2.913	3.8
3	3.027	8.6
4	3.109	13.2
5	3.165	16.0
6	3.210	19.3
7	3.263	22.8
8	3.294	25.9
9	3.297	27.6
10	3.308	30.1

Note: 100 ml. of methylene iodide and 100 ml of dimethyl formamide used for each test. Initial density of methylene iodide 3.296 g/ml. Each liter of wash water shaken for 10 minutes. Conditions otherwise as for washing tests.

Although Tests 7 to 11 show that increased washing times can affect the density in the third decimal place, the markedly increased losses make such washing times uneconomic.

A comparative test with methylene iodide and dimethyl formamide, carried out by shaking with successive liters of water, gave the results shown in Table 3. They show that very nearly the full theoretical amount of methylene iodide was dissolved, the total losses to attain a density of >3.3 g/ml being some 25 times those using the apparatus detailed above, and of the same order as losses on recovery detailed by Turner (1966).

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