The Solvent Extraction of Group IIIB Metal Halides

By H. M. IRVING and F. J. C. ROSSOTTI

SUMMARY

With the aid of the radio-nuclides ^{72}Ga, ^{114}In and ^{204}Tl, the extraction by ether of gallium bromide and iodide, indium chloride and iodide, thallic iodide, and thallous chloride, bromide and iodide from the corresponding halogen acids has been studied for a range of acid normalities. Liquid counting was used throughout. Although a simple density correction proved adequate with the pure β-emitter thallium, a special procedure had to be devised for gallium and indium to correct for variations in the counting rate with changes in the average atomic number of the nuclear species present in solution. The new data supplements existing information on the extraction of metal halides and confirms the prediction that indium iodide can be extracted quantitatively from hydriodic acid of low normality (0·5 to 2·5 N), where the extraction of gallium iodide is negligible. Potassium bromide, cyanide or fluoride, citric acid and di-sodium hydrogen phosphate in concentrations up to 0·5 M do not reduce the efficiency of extraction, but chloride ions have a slight effect, the percentage of indium extracted from 1·5 M hydrochloric acid made 1·5 M with respect to potassium iodide falling to 99·5 per cent.

The extraction by ether of ferrous and beryllium iodides from 1·5 M hydriodic acid was found to be essentially zero, so that a simple procedure for the determination of indium in the presence of gallium, iron and beryllium (among other metals) can be based on the solvent extraction of indium iodide. It is shown that free hydriodic acid can be conveniently replaced by sulphuric acid (1 to 7 N) containing sufficient potassium iodide to give a concentration of 1·5 M, and a preliminary spectrographic survey has been made of other elements whose iodides might be extracted by ether under these conditions.

RÉSUMÉ

On fait une étude de l'extraction par l'éther du bromure et iodure de gallium, du chlorure et iodure d'indium, de l'iodure thallique et du chlorure, bromure et iodure thalleux des acides halogénés correspondants, ayant une gamme de normalités, à l'aide des radio-éléments ^{72}Ga, ^{114}In, ^{204}Tl, et en utilisant un compteur pour liquides. Tandis qu'une simple correction de densité est suffisante pour le thallium, un émetteur pur de particules β, il a fallu mettre au point un procédé spécial pour le gallium et l'indium pour corriger les variations de la vitesse de comptage correspondant aux changements du nombre atomique moyen des espèces présentes dans la solution. Ces nouvelles données supplémentent les faits connus relatifs à l'extraction des haloïdes métalliques et confirment la prédiction qu'il est possible d'extraire complètement l'iodure d'indium de l'acide iodhydrique de faible normalité (0,5 à 2,5 N), dans lequel l'extraction de l'iodure de gallium est négligeable. Le rendement de l'extraction n'est pas amoindri par le bromure, cyanure ou fluorure de potassium, par l'acide citrique et par le phosphate neutre de sodium jusqu'à 0,5 M, mais le chlorure a un léger effet, le pourcentage d'indium extrait de l'acide chlorhydrique 1,5 M rendu, 1,5 M en iodure de potassium décroissant jusqu'à 99,5%.

On trouve que l'extraction de l'iodure ferreux et de béryllium de l'acide iodhydrique 1,5 M est sensiblement nulle, de sorte que l'on peut construire un procédé simple pour le dosage de l'indium en présence (entre autres) du gallium, du fer et du béryllium basé sur l'extraction de l'iodure d'indium par un solvant.

On démontre qu'il est commode de remplacer l'acide iodhydrique par l'acide sulfurique (de 1 à 7 N) contenant 1,5 M d'iodure de potassium, et on rend compte d'une étude spectrographique préliminaire d'autres éléments dont les iodures pourraient être extraits par l'éther dans des conditions semblables.

ZUSAMMENFASSUNG

Mit Hilfe der Radioelemente ^{72}Ga, ^{114}In und ^{204}Tl wurde die Aetherextraktion von Galliumbromid und Galliumjodid, von Indiumbromid und Indiumjodid, sowie von Thalliumjodid, Thalliumchlorür, Thalliumbromür und Thalliumjodür aus den entsprechenden Halogenwasserstoffsäuren für eine Reihe von Säurenormalitäten untersucht. In allen Fällen wurde die Auszählung der Flüssigkeiten angewandt. Während eine einfache Korrektur der Dichte im Falle des Thalliums genügte, das ein reiner β-Strahler ist, musste ein besonderes Verfahren für Gallium und Indium ausgearbeitet werden, um die Abweichungen in der Zählerrate auszugleichen, die mit den Unterschieden der mittleren Atomzahl der in der Lösung vorhandenen Arten zusammenhängen. Die erholtenen Ergebnisse ergänzen das bereits über die Extraktion von Metallhalogeniden Bekannte und bestätigen die Annahme, dass Indiumjodid quantitativ aus Jodwasserstoffsäure geringer Normalität (0,5 bis 2,5 N) extrahiert werden kann, während unter diesen Bedingungen Galliumjodid kaum extrahierbar ist. Kaliumbromid, Kaliumcyanid, Kaliumfluorid, Zitronensäure, Dinatriumhydrogenphosphat in Konzentrationen bis hinauf zu 0,5 M beeinträchtigen die Extraktion nicht, aber Chloridionen beeinflussen sie etwas. Indium lässt sich aus 1,5 M Salzsäure, die auch 1,5 M an Kaliumjodid ist, nur zu 99,5 Prozent extrahieren.

Es wurde gefunden, dass die Aetherextraktion von Eisenjodid und Berylliumjodid aus 1,5 M Jodwasserstoffsäure praktisch ergebnislos war, so dass eine einfache Methode für die Indiumbestimmung in Gegenwart von Gallium, Eisen und Beryllium (nebst anderen Metallen) auf der Extraktion von Indiumjodid aus Lösungen aufgebaut werden kann. Es wurde gefunden, dass freie Jodwasserstoffsäure bequem durch Schwefelsäure (1 bis 7 N) ersetzt werden kann, die auch an Kaliumjodid 1,5 M ist; spektrographische Untersuchungen anderer Elemente wurden angestellt, deren Jodide unter ähnlichen Bedingungen eine Bestimmung durch Aetherextraktion erlauben würden.

THE element indium is about as "rare" as platinum, but it never occurs free in nature and is seldom present to more than 0·1 per cent. in any of its ores. Interest in its chemistry has been stimulated by the fact that it has the third largest capture cross-section for thermal neutrons, so that its presence in materials to be used as neutron moderators or reflectors, e.g., beryllium,[1] cannot be tolerated. Further, as it is finding increasing industrial use,[2] its determination in, and separation from, a variety of other elements presents problems of some interest.

By making use of a Spekker absorptiometer fitted with a mercury lamp and filters to isolate the 4047 A line, the determination of microgram quantities by a solvent extraction technique involving 5:7-dichloro-8-hydroxyquinoline has been found[3] to be more sensitive than the well-known oxine procedure devised by Moeller,[4] though a number of metals interfere, especially vanadium[V], mercury[I], iron[III], gallium[III], molybdenum[VI] and copper[II]. However, the precipitation of microgram quantities of indium invariably requires a carrier and, in order to reduce contamination, cycles of re-solution and scavenging may be necessary. Thus, in the separation of fission products, indium has been precipitated with cadmium as sulphide and separated from it as basic acetate, but chemical yields of only 50 to 60 per cent. are reported.[5] A more elaborate procedure was adopted by Martell and Libby[6] when studying the natural β-activity of indium-115, and the process recently described for the extraction and purification of indium at La Oroya (Peru) from metals containing mainly tin and lead is excessively lengthy and complicated, and correction for inevitable losses has to be made by comparison with the results of an analysis of a sample to which a known weight of indium has been added.[7] Similarly, in separations from iron, Mathers and Prichard[8] found that some 4 per cent. of indium was co-precipitated with ferric cupferrate.

Errors due to co-precipitation and incomplete precipitation can often be eliminated when solvent extraction of a suitable complex is practised. Thus May and Hoffman[9] extracted

indium together with other metals as their oxinates into chloroform and, after decomposing these chelates, re-extracted indium from an alkaline citrate and tartrate medium with chloroform containing both dithizone and cupferron; losses of indium of up to 8 per cent. were still reported. More recently Milner has described a procedure in which indium and iron are separated from beryllium by extraction into chloroform as oxinates; after these have been decomposed, ferric chloride is extracted from concentrated hydrochloric acid into ether and the indium, which remains, is determined polarographically.[10] However, despite these demonstrations of the value of organic chelating agents, it was felt that the analytical potentialities of solvent extraction of simple inorganic compounds of indium had not been sufficiently explored for, as pointed out in a recent review,[11] such inorganic systems often exhibit striking peculiarities that lend themselves to separation procedures of outstanding selectivity.

Published work on the solvent extraction of indium compounds is meagre, and although data on other compounds of Group III metals are extensive, they are far from complete. While it is always difficult to make exact comparison of figures from different workers who may have employed different phase-ratios, concentrations of metals, or conditions of pre-saturation (q.v.), it appears that diethyl ether will extract no aluminium from 6 N hydrochloric acid but will remove ferric iron and gallium almost quantitatively; indium is extracted only in traces, and tervalent thallium almost completely. From 6 N hydrobromic acid, however, about 50 per cent. of the iron and gallium are extracted, whilst indium and thallium appear to be almost completely extracted.[11] If these trends in behaviour shown by the chlorides and bromides were continued with the iodides, the extraction of gallium should be much less than 50 per cent., although indium might still be extracted quantitatively. A further point of great significance is that the strength of acid from which maximum extraction takes place appears to be less for hydrobromic than for hydrochloric acid (see Figs. 3 and 4). If this trend also were continued with the iodides, we might find that the extraction of indium could be made complete from hydriodic acid of quite low normality, where the extraction of gallium would be negligible. Further, owing to the oxidising action of the ferric ion upon the easily oxidisable iodide ion, ferric iodide cannot exist in aqueous solution; and unless ferrous iodide differs materially from ferrous chloride, its extractability should be negligible, so that a separation of indium from iron and gallium, and probably from beryllium and aluminium among other elements, might be readily achieved. This supposition has proved to be correct.

While this work was in progress we became aware of a paper by Kitahara[12] reporting the extractability of metal iodides from 6·9 N hydriodic acid as follows: Be, Al, Ga and Fe^{II}, all 0 per cent.; Te^{IV}, 5·5 per cent.; Mo^{VI}, 6·5 per cent.; In, 7·9 per cent.; Zn, 10·6 per cent.; Bi 34·2 per cent.; Cd, Hg^{II}, Sn^{II} and Sb^{III}, all 100 per cent. An ether to water phase-ratio of 20 to 5 was used, but it is not clear whether the solvents were pre-treated in any way. The same author has recently published data on the solvent extraction of fluorides[13] as follows: Ag, Bi, Cd, Co, Cr, K, Ga, Mn, Ni, Os, Te, Ti, U, and Zr, all 0 per cent.; Sb, 0·4 per cent.; Se, 5·1 per cent.; As, 62·1 per cent.; Mo, 97 per cent.; Sn^{II} and Sn^{IV}, 100 per cent. In this case the strength of acid used is not known.

PARTITION EQUILIBRIA AND THE USE OF RADIO-NUCLIDES

When a metal halide dissolved in a halogen acid is shaken with ether, a complicated sequence of reactions ensues. Some of the metal is transferred to the organic phase, carrying with it halogen acid and water, often in stoicheiometric proportions. The solvents mix to some extent and there may be striking changes in the volumes of the phases; under certain circumstances even a third liquid phase may appear. In no single instance have these changes been completely interpreted.[11]

Fig. 1 shows how the extent of the changes in volume after equilibration of organic and aqueous phases (initially 20 ml each of ether and halogen acid—neither pre-treated in any way) increases with the strength of the halogen acid, and in the order HCl < HBr < HI. One important consequence of the volume changes and the partition of halogen acid is that the final normality, N', of the aqueous phase will be less than the initial value, N, as shown in Fig. 2. With increasing initial strength, N, the final normality, N', reaches and passes a maximum value (in the order HI < HBr < HCl) so that extraction cannot be carried out from acids stronger than about 5 N hydrochloric acid, 3·5 N hydrobromic acid or 2 N hydriodic acid unless the organic phase is pre-treated ("conditioned") with strong acid before equilibration. It will now be obvious how a major difficulty arises in correlating the values of

percentage extractions (q.v.) reported by workers who may have used different initial phase ratios or different degrees of pre-saturation. The volume and normality changes shown in Figs. 1 and 2 refer to the extraction of thallium[I] at a concentration of 2·68 mg per litre. Data obtained for other Group IIIB halides at the concentrations used in our experiments (q.v.) reproduce the same general features.

While academic interest will focus on the determination of the composition of the actual ion species or substances undergoing partition, and attempts would be made to compute the
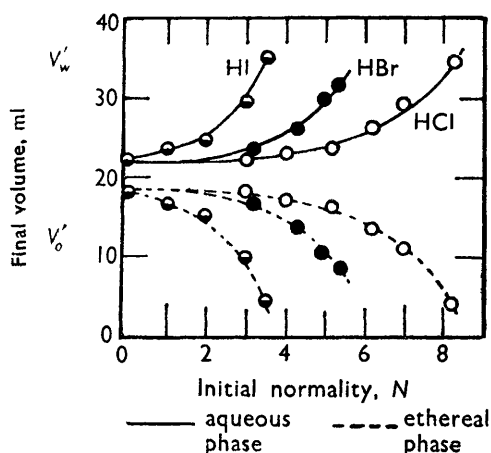

Fig. 1.   Volume changes on equilibrating equal volumes of ether and halogen acids of various strengths
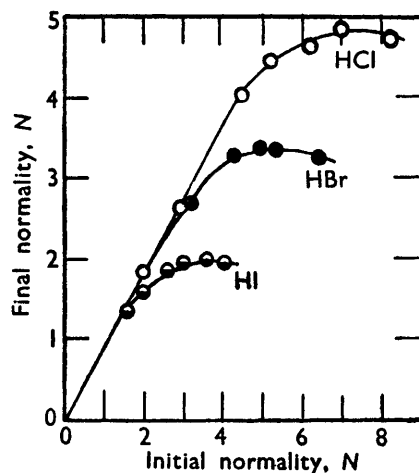

Fig. 2.   Final normality, N', after equilibration, as a function of initial normalities, N

relevant partition coefficients, the analyst is primarily interested in the gross distribution of an element between the two phases as expressed by a distribution coefficient defined by—

$$d = [M]'_o / [M]'_w \quad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad (1)$$

and the percentage of extraction defined by—

$$E = \frac{100\,V'_o[M]'_o}{V'_o[M]'_o + V'_w[M]'_w} = \frac{100}{(1 + V'_w/V'_o d)}, \quad .. \qquad .. \qquad .. \qquad (2)$$

where [M] denotes the *total* concentration of the element in any form, V denotes a phase volume, the subscripts o and w refer to organic and aqueous phases, and a superscript dash is used to distinguish the value of any parameter after equilibration.

It will be obvious that radionuclides are especially suitable for measurements of d and E, for if C_w, C'_w and C'_o are counting rates (corrected for background, paralysis-time, self-absorption and decay) for aliquots of the original aqueous phase before equilibration, and of the final aqueous and organic phases, then—

$$[M]_w : [M]'_w : [M]'_o = C_w : C'_w : C' \quad \cdot \quad .. \qquad .. \qquad .. \qquad (3)$$

$$\text{and } V_w[M]_w = V'_w[M]'_w + V'_o[M]'_o. \quad .. \qquad .. \qquad .. \qquad .. \qquad (4)$$

Equation (4) enables a mass-balance to be checked for each equilibration and from equations (1), (2), (3) and (4), d and E are readily found in terms of experimentally determinable values.

PROBLEMS OF RADIOCHEMICAL ASSAY

Though extensively used in studying solvent extraction of metal chelates, radio-nuclides have been much less frequently used with purely inorganic compounds. The first use of radioactive tracers for studying solvent extraction was the classical work of Grahame and Seaborg[14] in 1938; with mixed radio-isotopes obtained by the bombardment of zinc with

deuterons, the distribution coefficient of gallium trichloride between ether and 6 N hydrochloric acid was shown to be substantially the same for metal concentrations of $10^{-12}M$ and 0·0016 M. More recently gallium-72 and iron-59 have been used in extensive studies of the extraction of their chlorides from isopropyl ether.[15] Knox and Spinks[16] used indium-115 in their survey of the extraction of indium chloride with a variety of organic solvents, but the details published permit of only qualitative comparison with the results of the present work.

Previous workers have used solid counting techniques, but the quantitative precipitation of radio-nuclides from solutions of such varied composition as those likely to be encountered in the work projected, in a reproducible form suitable for precision counting, would be difficult and time-consuming when we bear in mind the importance of such factors as self-absorption and self-scattering in samples that are not "weightless." Direct counting of liquid samples on trays in a Geiger - Müller assembly with reproducible geometry[17,18] proved unsuitable for our strongly acid solutions containing ether. Indeed, liquid counting presents its own special problems, which may explain why, despite their obvious convenience, liquid counters have only been extensively used in biological and similar fields where measurements of moderate precision have been sufficient. However, it was felt that commercial Veall-type liquid counters[19] should be capable of adequate precision if a suitably designed technique were used, for constant geometry, at least, is imposed by their design.

The direct assay of ethereal and aqueous phases was not, of course, practicable in view of the known dependence of counting efficiency upon the electron-density and composition of the sample solution and the type and energy of the products of disintegration.[20] Fortunately thallium-204 is a pure β-emitter (0·775 meV), and the relationship between counting rate and solution density determined experimentally for various initial concentrations of radio-nuclide was found to be linear. But since the absorption of β-rays by the glass envelope of a Geiger tube (20th Century Electronic, Type M 6) depends on its thickness (the wall-thickness is about 30 mg per sq. cm) individual calibration curves were necessary for each counter.[20] If ρ g per ml is the solution density and C_c the counting rate corrected for background and paralysis time, the equation $[M] = C_c/[5750 - 3390\,(\rho - 1)]$ mg per litre was found to hold for counter No. 8675 up to $\rho = 1.25$. A few measurements were made with counter No. 1162, for which the appropriate equation was $[M] = C_c/[4010 - 3430(\rho - 1)]$ mg per litre for densities less than 1·15 g per ml. These counters were not actually used with solutions of density greater than 1·14 and 1·10, respectively. Equations previously proposed for counting rate - density corrections have included the logarithm of the former,[19,21] but these showed no advantages here over the linear relationship quoted.

With indium-114, which is essentially a γ-emitter (0·192, 0·552, 0·772 and 1·27 meV), preliminary measurements gave a smooth calibration curve for solutions in hydrochloric acid up to a density of 1·18 (11·5 N). When the composition of the solution was greatly varied in average atomic number as well as in electron density[20] (by the addition of salts such as calcium chloride, potassium iodide or indium sulphate) the scatter was such as to cause us to reject any form of density correction in favour of a technique that would be of general applicability.

Our problem, in short, is to collect microgram quantities of indium from an aqueous or organic solution containing varying amounts of halogen acids and inorganic salts, and to transfer it quantitatively for counting to a liquid phase that will always have exactly the same composition. A possible solution would be to add to the sample a large known excess of inactive indium, to precipitate the whole quantitatively and, after separation from mother liquors, to redissolve the precipitate in a suitable solvent. Such solutions will have essentially identical compositions and density, and will differ only in the insignificant proportion of radio-nuclide that is present. The form selected for precipitation was the *tris*-chelate complex formed with 8-hydroxyquinoline, and 2 N hydrochloric acid was chosen as the solvent. It is known[22] that indium oxinate, $InOx_3$, is quantitatively precipitated over the range pH 3·0 to 5·0. Aluminium oxinate, $AlOx_3$, which is very similar, begins to precipitate somewhat earlier, at pH 2·8, and the process is said to be quantitative[23] over the range pH 4·2 to 9·8, so that aluminium could be used with advantage as the carrier, apart from the advantage of cheapness. It will be appreciated that quantitative precipitation is not essential as long as the *fraction* of activity precipitated is the same in all determinations, but control experiments proved that, with the proportions actually adopted (q.v.), at least 99·6 per cent. of the total indium was precipitated with the aluminium oxinate. Details of the simple and flexible

procedure are given in the following section, and the method was found to be equally satisfactory for the determination of the gallium content of organic or aqueous phases. But although a *tris*-8-hydroxyquinoline complex of tervalent thallium, $TlOx_3$, has been prepared,[24] its precipitation could not be made complete under the conditions we used, and for this element, density corrections were made with the aid of calibration curves as described above.

Corrections for paralysis time were found to be negligible up to 10,000 counts per minute, and the statistical error of counting was kept low by counting for periods long enough to ensure a standard deviation of 1 per cent. or less. "Memory" effects were small with the procedure used for gallium and indium, and it was easy to restore the background count to approximately 13 per minute by washing successively with 2 N hydrochloric acid, with water, and then with alcohol, followed by air drying. Radio-thallium showed a greater tendency to become adsorbed, and concentrated sulphuric acid was found empirically to be more effective than other acids and oxidising agents for cleaning the counter. For each extraction experiment, C_w, C'_w and C'_o were always determined one after the other to minimise errors due to changes in counter efficiency. Some of the Veall-type liquid counters we have used have been markedly photo-sensitive. Throughout we have found it imperative to pay the greatest attention to the cleanliness of the mercury contacts to the two electrodes, as changes in contact resistance effectively change the applied potential so that the Geiger - Müller tube is operated on a different part of its plateau; this is seldom as flat or as long as could be desired and spurious changes in counting rate may appear if this detail is not most carefully checked.

To extend the data obtained with radio-nuclides on the solvent extraction of Group IIIB metal halides, the ether extraction of ferrous and beryllium iodides was investigated, absorptiometric and fluorimetric techniques, respectively, being used to determine the percentage of metal extracted.

METHOD

REAGENTS—

Technical diethyl ether was tested for the absence of peroxides and used without further purification. Laboratory grade chemicals were used in all distribution studies, but AnalaR grade reagents and solvents redistilled from an all-Pyrex glass apparatus were used when examining the effects of non-radioactive materials. Hydriodic acid was freshly distilled over phosphorus in an atmosphere of nitrogen within a day of using and stored in the dark.

RADIO-NUCLIDES—

Gallium-72; *half-life* 14·1 *hours*—A sample of "Specpure Ga_2O_3" from Messrs. Johnson Matthey could only be brought into solution after fusion with sodium carbonate. However, oxide from New Metals Ltd. proved less refractory and, after irradiation overnight in a flux of 9 × 10^{11} neutrons per sq. cm per second at A.E.R.E., Harwell, a sample of known weight (0·010 g) dissolved completely in 10 N sulphuric acid within half an hour. After cooling, the solution was made up to 100 ml with water to give a stock solution containing 74·4 mg of gallium-72 per litre in N sulphuric acid. Experiments with hydriodic acid were carried out with concentrations of 0·744 mg per litre, those with hydrobromic acid at 14·9 mg per litre.

Indium-114; *half-life* 48 *days*—Portions of "Specpure" indium wire of known weight were irradiated for four to eight weeks at 8 × 10^{11} neutrons per sq. cm per second. Solution in hot 10 N sulphuric acid was complete in 12 hours and a stock solution containing 5·0 g of indium-114 per litre in 2 N sulphuric acid was prepared. In studying extractions from hydriodic and hydrochloric acid a concentration of 30 mg per litre was used, but some experiments were carried out at a concentration of 0·615 mg per litre with a nuclide of higher specific activity.

Thallium-204; *half-life* 2·7 *years*—The material supplied by Harwell consisted of 97 per cent. of thallous nitrate together with 3 per cent. of insoluble matter, which was probably thallic oxide. A weighed quantity of high specific activity was dissolved in dilute nitric acid, filtered through sintered glass and diluted to give a stock solution containing 5·36 g of thallium-204 per litre in 0·1 N nitric acid. Tervalent thallium was prepared as required by oxidation with bromine water, any excess of which was removed with ammonium hydroxide. A concentration of 4·29 mg per litre was used for extractions of thallic iodide, and a concentration of 2·68 mg per litre was used in studying the extraction of thallous chloride, bromide and iodide.

GENERAL PROCEDURE—

To secure the maximum amount of analytically useful information, ether and solutions of metal halides in halogen acids were not submitted to any form of pre-saturation treatment, and the phase-volumes, metal concentrations and acid normalities were determined both before and after the equilibration.

Exactly 20·00 ml of ether and 20·00 ml of metal halide dissolved in halogen acid of the desired strength, N, were introduced by calibrated pipettes into a 60-ml Pyrex-glass test-tube fitted with a B24 ground-in stopper. After mechanical shaking for five minutes at 150 cycles per minute at room temperature ($14° \pm 2°$ C), the phases were allowed to separate completely. Centrifugation was never necessary. This time and degree of shaking was shown to be adequate for the attainment of equilibrium in selected systems only, but was almost certainly adequate in every system studied (*cf.* Nachtrieb and Fryxell[15]). With the tubes vertical, the levels of the menisci were noted on paper strips stuck to the outside of the tube. (After the tube had been emptied, cleaned, and dried, water was introduced up to these marks from a burette. This simple method enabled V'_w and V'_o to be measured with a standard deviation of $\pm 0·5$ per cent.) Aliquots of the two phases were then removed with pipettes for assay, care being taken to avoid contaminating one phase with the other.

ANALYSIS OF THE PHASES—

Indium extractions—A 10-ml portion of the aqueous phase was transferred by pipette into a 60-ml centrifuge tube and dissolved ether was removed by standing the tube in a bath of boiling water. Control experiments showed that no activity was lost in this procedure. The solution was then neutralised to methyl red with sodium hydroxide of a suitable strength (up to 10 N), the volume of alkali required being used to calculate N', the concentration of acid after equilibration. Ten milligrams of aluminium and an excess of oxine were then added as 10 ml of a "precipitating solution" prepared from 16·0 g of potash alum and 25·0 g of 8-hydroxyquinoline by dissolving and making up to 1 litre with 2 N hydrochloric acid. A drop of "Teepol" was then added and 10 ml of saturated sodium acetate solution run in slowly from a pipette. The yellow precipitate of metal oxinates was allowed to coagulate for 2 minutes at 100° C before being cooled and centrifuged. Supernatant liquid was then removed as completely as possible with a pipette and shown to be free from radioactivity. (Had any been present, a further precipitation could have been carried out.) After washing, 10 ml of 2 N hydrochloric acid was added to the precipitate and the centrifuge tube was placed in a bath of boiling water until solution was complete. After cooling, the liquid was transferred to a 25-ml flask and the centrifuge tube was rinsed several times with 2 N hydrochloric acid and the washings used to make the volume up to the mark. A 10-ml aliquot was then assayed in the G.M.6 assembly. The acid normality and metal content of a 10-ml aliquot of the aqueous phase before equilibration was determined in the same way, save that no ether had to be removed. In analysing the organic phase the neutralisation stage could be omitted, but the "precipitating solution" was then added as a hold-back carrier before the ether was evaporated. All experiments were carried out in duplicate and agreement was exceptionally good. Over-all mass-balances of 99·5 $\pm$ 4·8 per cent. were attained for all the extractions with indium chloride. Values of d when extraction approaches 0 or 100 per cent. are naturally particularly sensitive to the values of $[M]'_w$ and $[M]'_o$ obtained experimentally.

Gallium extractions—Analyses of phases were carried out exactly as described for indium and the appropriate correction was applied for radioactive decay. The isotope used was found to decay with a half-life of 14·1 hours and there were no long-lived impurities. Mass-balances in the extraction of gallium iodide were 100·2 $\pm$ 5·2 per cent.

Thallium extractions—Ten-millilitre aliquots of aqueous or organic phase were transferred to 25-ml standard flasks and, after the addition of 10 ml of 2 N hydrochloric acid (in chloride extractions) or 2 N nitric acid (for bromides or iodides), ether and any free halogen was removed on a bath of boiling water. Control experiments showed that there was no loss of activity in this ebullition stage. After cooling the volume was made up to 25 ml with the 2 N acid, a 10-ml aliquot was removed for counting and the density of the remainder measured to four significant figures with a Westphal balance. The acid normalities of further 10-ml aliquots of the aqueous phases before and after equilibration were determined by neutralisation with standard alkali to give N and N'. Counts were corrected for background and then

for density by using the appropriate equation determined experimentally beforehand (see p. 805). Mass balances of 101 ± 2.5 per cent. were obtained in the extraction of thallic iodide.

The extraction of ferrous iodide—Solutions of ferrous ammonium sulphate in hydriodic acid of various strength were made up to have an iron content of 12 g per litre. Ten-milli-litre portions were equilibrated (in duplicate) in the usual way with an equal volume of ether. To 2·5-ml aliquots of the ethereal phase after extraction was added 1 ml of concentrated nitric acid and, after removing the ether on a bath of warm water, iodide was removed by heating almost to dryness under an infra-red lamp. The residue was dissolved in water, transferred quantitatively to a 25-ml flask and reduced by the addition of 1 ml of 10 per cent. hydroxylamine hydrochloride solution. The pH was then brought within the range 3 to 6 with 40 per cent. sodium acetate solution and, after the addition of 1 ml of a 0·5 per cent. solution of 1:10-phenanthroline, the volume was made up to 25 ml and the absorbtion measured in a 1-cm cell with a Spekker absorptiometer fitted with a tungsten lamp and Ilford filter No. 604. Specially purified reagents and scrupulously cleaned apparatus was used, and controls were run in duplicate. The concentration of iron in the ethereal extracts was then determined with reference to calibration curves for known amounts of iron taken through the same procedure.[25] The results are shown in Table I.

TABLE I

THE EXTRACTABILITY BY DIETHYL ETHER OF METAL HALIDES FROM SOLUTIONS IN HALOGEN ACIDS

Indium chloride (30 mg per litre)

N	E	d
4·0	0·59	0·001
5·0	1·45	0·022
6·0	2·53	0·05
7·0	4·13*	0·13
8·0	3·02*	0·24
10·5	5·27†	0·20

Indium iodide (3 g per litre)

N	E	d
0·15	34·6	0·58
0·50	99·5	248·0
2·5	99·3	264·0
3·41	71·2	12·9

(30 mg per litre)

N	E	d
0·07	2·59	0·037
0·12	33·3	0·62
0·16	56·8	1·60
0·23	75·8	4·02
0·53	98·8	101·0
1·06	99·9	1770·0
2·02	99·9	1530·0
2·63	98·8	150·0
3·03	90·5	26·8
3·50	60·1	6·3
4·16	19·6*	0·86
5·10	7·4‡	0·41
6·80	1·4§	0·18

(0·6145 mg per litre)

N	E	d
0·10	39·2	0·80
0·25	94·0	17·1
0·49	99·4	211·0
1·55	99·9	1033·0
2·05	99·3	246·0
2·50	96·0	54·8
3·15	48·5	4·92
3·50	37·7	3·37

Gallium bromide (14·9 mg per litre)

N	E	d
3·0	0·49	0·0084
3·5	3·7	0·068
4·0	16·9	0·44
4·5	40·4	1·93
5·0	28·9	1·74
5·5	11·8	0·92
6·0	8·9*	0·41

Gallium iodide (0·744 mg per litre)

N	E	d
0·11	0	0
2·00	0	0
3·82	0·1	0·005
5·86	1·2‖	0·15

Thallic iodide (4·29 mg per litre)

N	E	d
0·012	86·5	8·29
0·051	99·8	496·0
0·102	99·9	814·0
0·51	∼100·0	1930·0
1·00	99·9	2700·0
2·02	99·5	345·0
2·59	96·2	61·0
3·10	69·5	8·86
3·48	9·27	1·92

Ferrous iodide (12 g per litre)

N	E	d
0·5	0·009	—
1·5	0·010	—
2·5	0·010	—

Beryllium iodide (4·66 g per litre)

N	E	d
0·5	0	—
1·5	0	—
2·5	0·008	—

Thallous chloride (2·68 mg per litre)

N	E	d
0·1	0	0
2·0	0·74	0·0089
3·08	2·65	0·033
4·48	3·55	0·050
5·20	5·25	0·078
6·19	7·66	0·163
7·08	2·98	0·080
8·27	0·66	0·057

Thallous iodide (2·68 mg per litre)

N	E	d
0·005	24·9	0·4
0·010	66·8	2·6
0·025	84·2	6·2
0·51	99·9	1470·0
1·57	99·8	647·0
2·03	99·6	436·0
2·54	99·0	212·0
3·05	82·0	14·1
3·55	22·7	3·18

Thallous bromide (2·68 mg per litre)

N	E	d
0·14	11·7	0·162
0·31	32·7	0·617
0·54	61·7	2·18
0·74	93·3	17·6
1·05	99·9	807·0
3·21	99·8	691·0
4·28	97·0	62·3
4·95	77·3	9·45
5·31	41·5	2·97
6·43	6·2	0·86

All concentrations refer to weights of metal per litre. Values for the phase ratio $V_o/V_w = 20/20$ except where indicated by the symbols * for 30/20; † for 20/10; ‡ for 40/20; § for 30/10 and ‖ for 50/20.

The extraction of beryllium iodide—A stock solution containing 7·77 g per litre was prepared by fusing 2·154 g of pure beryllium oxide with sodium pyrophosphate and taking up the melt in 0·1 N sulphuric acid.   Solutions in hydriodic acid of various strengths were then prepared, all containing 4·66 g of beryllium per litre together with considerable amounts of sodium sulphate, which would be expected to increase the percentage extraction in view of the probable salting-out effect.[11]   Equilibrations with an equal volume of ether were performed in duplicate and 5-ml aliquots of the ethereal phase were then treated with 1 ml of concentrated nitric acid, and ether and hydriodic acid was removed as in the experiments with iron. The residue was taken up in 5 ml of 0·2 N sodium hydroxide and 5 ml of saturated sodium pyrophosphate and, after the addition of 0·2 ml of a solution of morin (3:5:7:2':4'-pentahydroxyflavone) in acetone, the fluorescence was compared with that of blanks and of similar solutions containing a known amount of beryllium.[25]   The results are shown in Table I.

DISCUSSION OF EXPERIMENTAL RESULTS

Table I summarises our main experimental results.   The values of V'_o and V'_s are not given, but their order of magnitude is indicated by Fig. 1.   The variation of percentage extraction with acid normality is shown in Figs. 3, 4, and 5, together with values for other
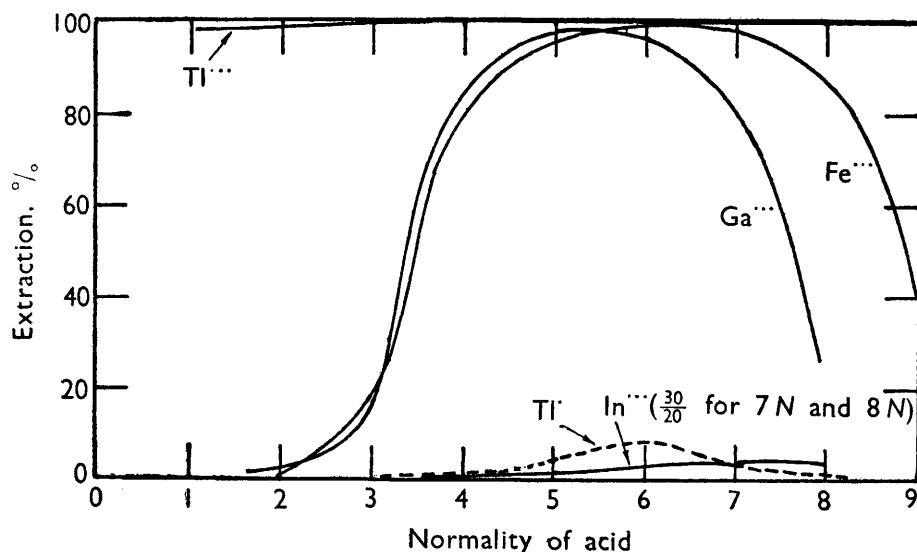

Fig. 3.   Extraction of chlorides from hydrochloric acid.   Ratios refer to V_o/V_w

metal halides, which are included for the sake of comparison.   The data of Swift[26] on gallium chloride, and of Dodson, Forney and Swift[27] on ferric chloride refer (like ours) to equal initial volumes of organic and aqueous phases, those of Wada and Ishii[28] for thallic chloride, and for gallium, indium, thallic and ferric bromides refer to the extraction of 20 ml of aqueous phase by 30 ml of pre-saturated organic phase.   Widely different metal concentrations have been used by these workers, always greater than our own; but although the numerical values are not therefore directly comparable, the general trends are unmistakeable.   The differences between our values for gallium bromide and those of Wada and Ishii[28] are in the direction and of the extent to be expected from the differences in phase-ratio and pre-treatments of solvents.

As predicted (p. 803), the extraction of indium iodide can be made quantitative (over the range 0·5 to 2·5 N hydriodic acid) under conditions where the extraction of gallium iodide is imperceptible.   It can be seen, too, that thallic iodide, like the bromide and chloride, is quantitatively extracted from very dilute acid, and that the extraction of small amounts of thallous iodide and bromide (but not chloride) can be made quantitative from the corresponding halogen acids of the appropriate normality.   For all the systems studied the percentage extraction increases with acid normality and passes through a maximum; and the acid normality at which this occurs is lower for bromides than for chlorides, and lower still for iodides.

This effect should be considered in relation to the maxima shown in Fig. 2, and it is shown more clearly in plots of log d against log N (not reproduced here), which will be discussed elsewhere in connection with a more general treatment of solvent extraction.   The variations in extractability among the halides of the Group IIIB metals are in just the order we should expect from the general chemistry of this group, and detailed correlation with the stabilities of the species concerned is under consideration.
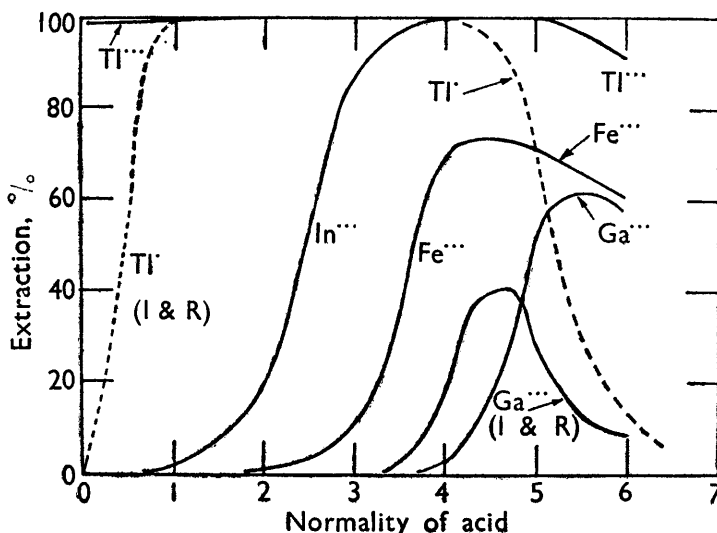

Fig. 4.   Extraction of bromides from hydrobromic acid.   (I. & R.—present work; all other measurements from Wada and Ishii.[28])   For phase-ratios see text
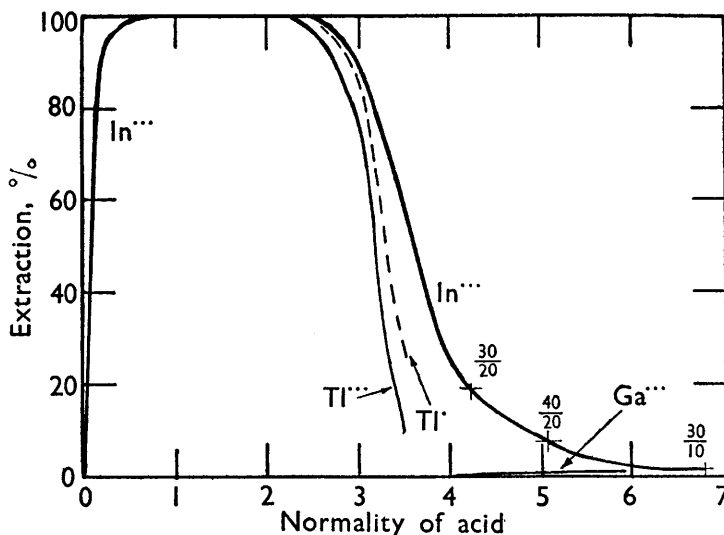

Fig. 5.   Extraction of iodides from hydriodic acid.   Ratios refer to V_o/V_w.
The value 50/20 for extraction of gallium iodide from 5·86 N
hydriodic acid is omitted for reasons of clarity in plotting

It is well known that the percentage of, e.g., iron or gallium chlorides extracted from acid of optimum normality decreases with the concentration of metal.[15,27]   Table I shows that this effect is not serious for indium iodide from 0·026 M down to 5·4 × 10^{-6} M.   The percentage extraction never falls below 99·9 per cent. at the acid normality for optimum extraction, which is 1·5 N.

A study of anions that might interfere with the extraction of indium iodide from $1 \cdot 5 \, N$ hydriodic acid showed that extractions were between 99·9 and 100 per cent. in the presence of 0·5 M potassium bromide, cyanide or fluoride, citric acid, or di-sodium hydrogen phosphate. The presence of 0·5 M potassium chloride reduced the extraction to 99·8 per cent., and this indication of slight interference by the chloride ion was confirmed by the figure of 99·5 per cent. for extraction of indium from $1 \cdot 5 \, N$ hydrochloric acid made $1 \cdot 5 \, M$ with respect to potassium iodide.

It will be obvious that the quantitative solvent extraction of indium iodide can be made the basis of analytical procedures for its separation from ferrous iron, beryllium, gallium and certainly many other elements. But the use of solutions of hydriodic acid introduces a number of undesirable features, as this acid decomposes so readily on keeping. However, the data shown in Tables II and III demonstrate that the free acid can be replaced with advantage by sulphuric acid to which the appropriate amount of potassium iodide has been added. Indeed the concentration of iodide, and more especially that of the acid, can be varied over quite wide limits without reducing the efficiency of extraction.

TABLE II

THE EXTRACTION* OF INDIUM FROM A 30-mg PER LITRE SOLUTION IN THE PRESENCE OF $1 \cdot 5 \, N$ SULPHURIC ACID

Molarity of added potassium iodide	0	0·15	0·5	1·0	1·62	3·5
Percentage extraction, E	0	70·6	99·3	99·7	99·8	99·9
Distribution coefficient, d	0	2·66	160·0	415·0	640·0	890·0

TABLE III

THE EXTRACTION* OF INDIUM FROM A 30-mg PER LITRE SOLUTION IN THE PRESENCE OF $1 \cdot 5 \, M$ POTASSIUM IODIDE

Normality of added sulphuric acid	0·01	0·02	0·10	0·23	0·50	7·0
Percentage extraction, E	96·8	98·4	99·4	99·7	99·8	100·0
Distribution coefficient, d	34·9	72·5	193·0	368·0	500·0	3510·0

* In these extractions $V_w = V_o = 20$ ml, $V'_w \simeq 22$ and $V'_i \simeq 18$ ml.

Further experiments have shown that the simultaneous variation of acid and iodide concentration presents a number of interesting features that cannot be discussed here, but for analytical purposes a mixture containing approximately 1·5 M potassium iodide in approximately 1·5 N sulphuric acid seems satisfactory. A preliminary spectrographic survey of the extent to which elements, outside Group IIIB, at a concentration of 1 g per litre, are extracted by diethyl ether from this particular acid - iodide mixture gave the following results, which should be compared with those of Kitahara[12] (p. 3) relating to 6·9 N hydriodic acid: Be and Fe^{II}, 0 per cent.; Al, <0·1 per cent.; Mo^{VI}, W^{VI}, <1·0 per cent.; Bi and Cu, <10 per cent.; Zn and Hg, about 33 per cent.; Sb, <50 per cent.; Cd and Sn^{II}, 100 per cent. Clearly a full appraisal of the potentialities afforded by the facile extraction of indium iodide as a selective procedure must await more extensive data relating to strictly comparable conditions of extraction. But there can be no doubt that the procedure offers considerable advantages over existing methods for the separation of traces of indium from other metals. Detailed procedures for the determination of indium in the presence of, e.g., iron, aluminium, gallium and beryllium will be presented elsewhere.

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DISCUSSION

MR. G. W. C. MILNER (Harwell) said that he had developed a method for the determination of indium in beryllium alloys (*Analyst*, 1951, **76**, 488) in which two separate solvent extraction procedures were used. The work of Dr. Irving and Mr. Rossotti now showed that this method could be considerably simplified. He asked whether the extraction of metal iodides by solvents other than diethyl ether had been examined.

With gallium chloride the maximum extraction occurred over a much wider range of acid strengths when diethyl ether was replaced by *iso*propyl ether. This flexibility introduced the possibility of analytical separations by suitable choice of acid strength. He asked if Dr. Irving would indicate whether a similar gain in flexibility in the choice of acid strengths would occur in the extraction of indium iodide if diethyl ether were replaced by *iso*propyl ether.

DR. IRVING replied that in all solvent extraction work there was a large number of variables to be considered, foremost among which were the behaviour of a large number of metals over wide ranges of concentration, the effects of change of solvent, of acidity in the aqueous phase and of the concentration and nature of salting-out agents. With the limited time available, Mr. Rossotti and he had concentrated on a reasonably thorough study of a few metal iodides with diethyl ether only as solvent, but the work was already being extended to other metals and other solvents. Data on the extraction of inorganic halides were too incomplete to attempt any very reliable answer to Mr. Milner's second question. However, it seemed reasonable to predict that on replacing diethyl ether by (say) *iso*propyl ether, maximum extraction of indium iodide would not occur until a greater concentration of hydriodic acid was used. This might prove troublesome in practice, owing to the increased ease of oxidation with the concomitant liberation and partition of iodine. Moreover, miscibility considerations (*cf.* Fig. 2 of the paper) also suggested that the practicable range of halogen acid concentrations decreased in the order hydrochloric > hydrobromic > hydriodic acid.

MR. H. BEHRENS asked if the same technique had been applied to carrier-free radio-nuclides and if so, what results had been indicated.

DR. IRVING replied that carrier-free isotopes had not been used so far in the work. Radio-nuclides had been used merely to "label" the metals concerned so as to facilitate measurements of distribution. The lowest concentration had been round about 1 p.p.m.