797. *A Neutron-activation Study of the Solubility of Mercury in Water.*

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A method has been developed for the neutron activation analysis of mercury in aqueous solution. The limits of sensitivity of the method are calculated, and it is shown that 10^{-9} g. of Hg can be detected. The method has been applied in studies of the solubility of mercury in water over the temperature range 25—90°. The preparation of completely air-free solutions, and the sampling and irradiation methods are described. The results, which show good internal agreement, are compared with other values in the literature.

Mercury has a number of properties which single it out from the other metals, and amongst these must be included its finite solubility in water at room temperature. This was first reported by Stock,[1] who later [2] discussed in detail some of the factors affecting the solubility; the experimental result reported for 30° was 0·02—0·03 μg./ml., with appreciably higher values at 85° and 100°. At about the same time, Reichart and Bonhoeffer [3] showed that the absorption spectrum of an aqueous solution of mercury was essentially the same as that of mercury vapour, except for line broadening which they ascribed to weak solvation effects. It is important to note that this work implies that the species present in the aqueous solutions are mercury atoms rather than ions or hydroxo-species. The solubility of mercury in water has also been measured by Pariaud and Archinard [4] who reported values similar to those found by Stock; these measurements were based essentially on colorimetric analysis by means of the mercury–dithizone complex. The most recent work is that by Moser and Voigt,[5] who brought water into contact with mercury labelled with ^{203}Hg and measured the specific activity, and hence mercury concentration, in the resultant equilibrium aqueous solution. This method necessitated a high activity in the mercury phase, and it was found that small amounts of hypophosphorous acid had to be added to the system to prevent radiolytic oxidation of the metal; it was shown that the results were unaffected by varying the concentration of the hypophosphorous acid over the range 0·1—0·001M.

We selected the neutron-activation method of analysing for mercury in the present work because of the high sensitivity and high specificity possible in the final analysis. It is shown below that the high sensitivity means that only very small volumes of solution need to be taken for analysis, and this accordingly simplifies the experimental procedure. In addition, since no chemical treatment of the mercury is required until after the sampling and neutron-activation procedure, this method avoids the slight uncertainty implicit in the presence of even very small amounts of reagents such as hypophosphorous acid in the

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[1] Stock, *Naturwiss.*, 1932, **20**, 954.
[2] Stock, Cucuel, Gerstner, Köhle, and Lux, *Z. anorg. Chem.*, 1934, **217**, 241.
[3] (*a*) Reichart and Bonhoeffer, *Z. Elektrochem.*, 1930, **36**, 753; (*b*) *Z. Phys.*, 1931, **67**, 780.
[4] Pariaud and Archinard, *Bull. Soc. chim. France*, 1952, 454.
[5] Moser and Voigt, *J. Amer. Chem. Soc.*, 1957, **79**, 1837.

aqueous solution during equilibration. It is surprising that, although there is a great deal of published work on neutron-activation analysis (Meinke[6] has listed over 1200 references up to 1958), only two reports[7,8] are concerned with mercury. One of these[8] discusses the difficulties of flux monitoring with solid standard mercury preparations, and we therefore decided to attempt the direct pile neutron-irradiation of liquid samples (and standards) in silica ampoules, which were tested before irradiation to withstand the expected internal pressure. When the present work was nearing completion, Westermark and Sjorstrand[9] described the application of a similar technique to the analysis of mercury in a wide variety of samples. However, these authors counted the mercury activity directly, with no chemical treatment of the irradiated sample, and this necessarily affects the minimum quantity of mercury that can be detected because of the presence of other activities.

Radiometric Analysis.—The selection of the most suitable radioactive isotope of the element in question, and of the appropriate radiometric technique, are most important in radioactivation analysis, since these factors often determine the overall sensitivity of the method; in particular, in the present work, the radiometric sensitivity governed the volume of solution to be irradiated. Table 1 gives the relevant nuclear data for those mercury isotopes which can be produced by slow neutron bombardment.

TABLE 1.

Mercury isotopes produced by (n,γ) reactions.

Target nuclide	Natural abundance (%) (*a*)	Product nuclide (*b*)	Neutron-activation cross-sections (barns)	Half-life of product nuclide (*c*)
^{196}Hg	0·146	^{197m}Hg	420 ± 80 (*d*)	24 hr.
		^{197}Hg	880 ± 75 (*d*)	65 hr.
^{198}Hg	10·02	^{199m}Hg	—	42 min.
^{202}Hg	29·80	^{203}Hg	3·8 ± 0·8 (*b*)	46·9 days
^{204}Hg	6·85	^{205}Hg	0·43 (*b*)	5·5 min.

(*a*) Ref. 10. (*b*) Ref. 11. (*c*) Ref. 12. (*d*) Ref. 13.

Hughes and Schwartz[11] give 3100 ± 100 b. for the total cross-section for $^{196}\text{Hg}(n,\gamma)^{197+197m}\text{Hg}$, while Westermark and Sjorstrand state that the activation cross-section for ^{197m}Hg production is about 100 times greater than that for ^{197}Hg. The figures given in the Table are used, however, both for convenience of calculation and because they give an upper limit for the sensitivity of the method.

An examination of Table 1 shows that ^{199m}Hg and ^{205}Hg are too short-lived for a neutron-activation procedure which involves appreciable time for transportation and subsequent chemical treatment. Furthermore, the activity I (d.p.m.) produced by the bombardment of x target atoms for a time t in a neutron flux Φ (n. cm.$^{-2}$ sec.$^{-1}$) is:

$$I = \Phi\sigma x[1 - \exp(-\lambda t)], \tag{1}$$

where σ is the activation cross-section and λ the decay constant of the isotope produced. It is clear from eqn. (1) that for a given bombardment time, ^{203}Hg will give a much lower activity than $^{197m+197}$Hg, so that the final determination of the activity was based on the latter pair of isomers. In addition to the normal time-dependent factors, there is a further reason for keeping the irradiation time to a minimum when dealing with liquids, namely, the prevention of excessive pressure build-up in the sealed ampoule as the result of radiolytic decomposition caused by the high γ-flux in the reactor.

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[6] Meinke, *Analyt. Chem.*, 1958, **30**, 686.

[7] Smales, Proc. 1st Internat. Conf. on Peaceful Uses of Atomic Energy, United Nations, Geneva, 1955, Vol. IX, p. 273.

[8] Ehmann and Huizenga, *Geochim. Cosmochim. Acta*, 1959, **17**, 125.

[9] Westermark and Sjorstrand, *Internat. J. Appl. Radiation Isotopes*, 1960, **9**, 1.

[10] Nier, *Phys. Rev.*, 1950, **79**, 450.

[11] Hughes and Schwartz, " Neutron Cross-Sections," U.S.A.E.C. report BNL–325 (1958).

[12] Strominger, Holland, and Seaborg, *Rev. Mod. Phys.*, 1958, **30**, 585.

[13] Sehgal, Hans, and Gill, *Nuclear Phys.*, 1959, **12**, 261.

The predominant features of the ^{197m}Hg $\longrightarrow$ ^{197}Hg $\longrightarrow$ ^{197}Au decay scheme[12] are: (i) ^{197m}Hg undergoes an isomeric transition (97%) to ^{197}Hg, emitting 0·134 Mev γ-radiation which is internally converted (66%). The *K X*-rays emitted as the result of internal conversion have an average energy of 68 Kev. (ii) ^{197}Hg goes to the first excited state of ^{197}Au by electron capture (99%). This therefore gives further *K X*-rays, plus the 77 Kev γ-ray emitted in the de-excitation of the excited ^{197}Au nucleus.

We therefore used a crystal spectrometer (see below) set to count only those pulses in the 68—77 Kev region.

Sensitivity of the Method.—The combination of eqn. (1) with the usual radioactive decay law gives the activity at a time θ after the end of the neutron bombardment. We can replace x by $w\mathbf{N}p/A$ where w is the mass of the element in question in the target, $\mathbf{N}$ Avagadro's number, A the atomic weight, and p the abundance of the isotope concerned, so that

$$I = \Phi\sigma \frac{w\mathbf{N}p}{A} (1 - e^{-\lambda t})(e^{\ \lambda\theta}). \qquad (2)$$

The highest neutron flux available to us was that of the BEPO reactor at A.E.R.E., Harwell, with a maximum flux of 1·2 × 10^{12} n. cm.$^{-2}$ sec.$^{-1}$. For convenience, we consider the bombardment of a 1 μg. sample of mercury metal for 1 week, with an interval of 65 hr. (=half-life of ^{197}Hg) before counting. The activities present at this time, as calculated from eqn. (2), are:

$$I_{(197m)} = 2{\cdot}03 \times 10^4 \text{ d.p.m. and } I_{(197)} = 1{\cdot}16 \times 10^5 \text{ d.p.m.}$$

for each of the two isomers produced.

Now ^{197}Hg is also formed by the decay of ^{197m}Hg during the period $(t + \theta)$. For a system represented by

$$\text{A} \xrightarrow{(n,\gamma)} \text{B} \xrightarrow{\lambda_\text{B}} \text{C} \xrightarrow{\lambda_\text{C}}$$

the classical Bateman[14,15] equations can be used[16] to calculate the activity of material C present a known time after the end of the neutron irradiation. Making the various simplifying assumptions possible for the time intervals assumed above, one has

$$I_\text{C} = \Phi\sigma_\text{A}x_\text{A}\left[\frac{\lambda_\text{C}}{\lambda_\text{C} - \lambda_\text{B}}(e^{-\lambda_\text{B}t} - e^{-\lambda_\text{C}t}) + \left(1 - \frac{\lambda_\text{B}}{\lambda_\text{B} - \lambda_\text{C}} \cdot e^{-\lambda_\text{C}\theta}\right)e^{-\lambda_\text{C}t}\right], \qquad (3)$$

and by substituting the appropriate values one finds that the ^{197}Hg activity produced by this route is

$$I'_{(197)} = 7{\cdot}55 \times 10^4 \text{ d.p.m.},$$

giving a total ^{197}Hg activity of 1·92 × 10^5 d.p.m.

It is now necessary to calculate the number of γ and *X*-ray quanta, with energies in the 68—77 Kev region, produced per 100 disintegrations of the two nuclides in question.

(i) Electron capture is almost entirely by *K*- or *L*-capture, with about 86% *K*-capture at $Z \approx 80$ (Rose and Jackson[17]). The fluorescence yield is 96% at this atomic number,[18,19] so that one obtains 82 *K X*-rays per 100 electron captures.

(ii) The details of internal conversion, etc., are shown in Table 2.

The total number of quanta in the 68—77 Kev band emitted by ^{197m}Hg and ^{197}Hg produced by neutron-irradiation under the conditions set out above is therefore:

$$^{197m}\text{Hg}: \ 2{\cdot}03 \times 10^4[(3 \times 0{\cdot}86 \times 0{\cdot}96) + 20{\cdot}7 + 15{\cdot}5] \times 10^{-2} = 7{\cdot}83 \times 10^3 \text{ d.p.m.}$$

$$^{197}\text{Hg}: \ 1{\cdot}92 \times 10^5[(99 \times 0{\cdot}86 \times 0{\cdot}96) + 0{\cdot}5 \times 29] \times 10^{-2} = 2{\cdot}14 \times 10^5 \text{ d.p.m.}$$

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[14] Bateman, *Proc. Cambridge Phil. Soc.*, 1910, **15**, 423.

[15] Rutherford, Chadwick, and Ellis, " Radiations from Radioactive Substances," Cambridge Univ. Press, 1951, p. 15.

[16] Crouthamel, " Applied Gamma-Ray Spectrometry," Pergamon Press, London, 1960.

[17] Rose and Jackson, *Phys. Rev.*, 1949, **76**, 1540.

[18] Broyles, Thomas, and Haynes, *Phys. Rev.*, 1953, **89**, 715.

[19] Gray, *Phys. Rev.*, 1956, **101**, 1306.

TABLE 2.

Low energy *X*- and γ-rays from ^{197m} + ^{197}Hg. (refs. 12, 20).

Nuclide	γ-Energy (Mev)	% unconverted	No. of *K X*-rays per γ	No. of 68—77 Kev quanta per 100 disintegrations
^{197m}Hg	0·164	4·5	4·6	20·7
	0·133	31	0·5	15·5
^{197}Hg	0·192	0·5	1	0·5
	0·077	29	0	29

In terms of calculating the limits of detection, the final activity of $2{\cdot}22 \times 10^5$ d.p.m. must be reduced by three factors: (i) Radiochemical purification in the final stage gives a chemical yield of about 70%. (ii) The efficiency of the scintillation crystal used is only about 40% (see refs. 21, 22). (iii) Escape of the iodine *K X*-ray from the scintillation crystal reduces the counting rate; we adopt the value of 10% loss suggested by Doerner and Weber.[23]

It follows then that a 1-week neutron-irradiation of 1 μg. of mercury in the maximum flux of BEPO should give a counting rate of 8×10^4 c.p.m. in the 68—77 Kev region with the counter used (see below). The background was found to be $\sim$55 c.p.m. and, if we accept twice background as a reasonable lower limit of detection, then the smallest amount of mercury which can be detected by this method is $\sim 2 \times 10^{-9}$ g. This could presumably be lowered in practice by careful statistical treatment of counting rates. It should also be noted that the value taken for the activation cross-section may well be too low (see footnote to Table 1). These calculations demonstrated the feasibility of the neutron activation method for the present work.

EXPERIMENTAL

Materials.—Spectroscopically pure mercury was obtained from Messrs. Johnson Matthey & Co.; the only detectable impurity was 1 p.p.m. of sodium.[24]

" Distilled water," triple distilled from fused silica vessels and condenser, was used in the preparation of sample and standard solutions, and also in steam-cleaning the apparatus (see below). In other parts of the work (*e.g.*, separation of the radioactive mercury), ion-exchanged water was used.

Standard solutions were made up from " AnalaR " mercuric chloride. All other materials were of " AnalaR " grade.

Preparation of Aqueous Solution of Mercury.—The solution must be prepared under air-free conditions, since atmospheric oxidation increases the amount of mercury in solution.[2] Thin-walled bulbs were therefore filled with mercury *in vacuo*, and these were placed in vessels into which water was distilled, again *in vacuo*. All the apparatus shown in Figs. 1 and 2 was of silica, save for traps, etc., to which connection was made *via* Pyrex–silica graded seals.

The mercury-containing bulbs were prepared in the apparatus shown schematically in Fig. 1. Before assembly, the individual parts were soaked for 2 days in a 1 : 1 mixture of concentrated nitric and sulphuric acid to leach out any soluble materials, then repeatedly rinsed with water; the use of chromic acid was avoided, since chromium may be irreversibly adsorbed on the walls.[25, 26] The bulbs B_1, etc., and tubes D and F, were left open after assembly of the apparatus in order that steam could be blown through them for 2—3 hr., after which D, F, and $B_1 \ldots B_5$ were closed off and the apparatus was tested for leaks under a high vacuum. A double series of liquid-air traps prevented diffusion of mercury, oil, etc., into the cleaned parts of the apparatus. After this test, the apparatus was opened to the atmosphere *via* the side tube D, into which was sealed a very fine glass sinter E to prevent dust being carried into

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[20] Joly, Brunner, Halter, and Hüber, *Helv. Phys. Acta*, 1955, **28**, 403.

[21] Bell, in " Beta- and Gamma-Ray Spectroscopy," ed. Siegbahn, North-Holland Publ. Co., Amsterdam, 1955, Chap. 5.

[22] Vegors, Marsden, and Heath, Philips Petroleum Co. Report IDO-16370 (1958).

[23] Doerner and Weber, *Phys. Rev.*, 1955, **99**, 672.

[24] Personal communication from Messrs. Johnson Matthey.

[25] Laug, *Ind. Eng. Chem.*, *Analyt.*, 1934, **6**, 11.

[26] Butler and Johnson, *Science*, 1954, **120**, 543.

the apparatus by the inrush of air when the tip of D was broken; this sinter also served to control the rate at which the air entered.

The filling tube F was then cut open, and about 6 ml. of "spec." pure mercury introduced into A with a clean silica dropper. The open ends of tubes E and F were closed, and the apparatus was again evacuated and tested for leaks. The whole silica part of the apparatus (except that part of A containing the mercury) was next heated strongly with a hand-torch to drive out any adsorbed oxygen; evacuation was continued until the pressure fell below 10^{-5} mm. Gentle heating of bulb A caused mercury to distil into B_1; heating was discontinued when about 1 ml. had condensed in B_1, which was sealed off at the constriction C; in this way, 4—5 mercury bulbs could be filled in a single experiment. Each bulb was finished off to have a small hook at the top so that it could be handled with a silica rod without being touched by hand. The surface of the bulb was rinsed, first with ethanol, and then several times with distilled water, immersed in water for 1 day, and stored in a clean beaker in a desiccator until required.

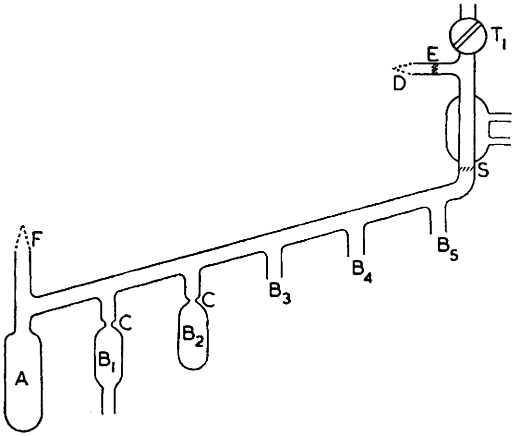

FIG. 1. Apparatus for filling mercury bulbs *in vacuo*.

A, Mercury reservoir; B_1, etc., tubes to be filled (B_1 before steam cleaning; B_2 after cleaning and sealing; final dimensions 3 cm. long, 0·8 cm. outside diameter); C, constriction; D, side-tube with sinter E; F, tube for filling A with mercury; S, silica–Pyrex graded seal; T_1, greaseless tap.

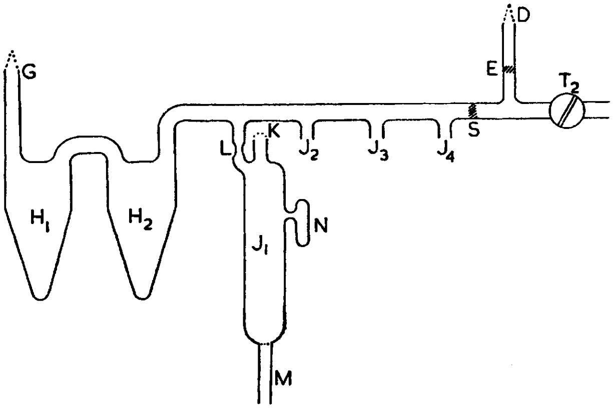

FIG. 2. Apparatus for preparing solutions of mercury in air-free water.

D, E, S, as in Fig. 1; H_1, H_2, pear-shaped bulbs, ~250 ml. volume; J_1, etc., sample tubes (final dimensions of sealed tube 10 cm. long, 2·5 cm. outside diameter); T_2, greaseless tap.

The apparatus for preparing the solutions is shown in Fig. 2. The apparatus was cleaned, assembled, steam-cleaned, sealed at K and M, tested for leaks under a vacuum, and then opened to the air *via* the sinter E as described above. A mercury bulb was then carefully introduced into each tube J_1, etc., through the opened tube K, which was sealed off. About 100 ml. of distilled water were placed in the pear-shaped flask H_1 through G, and tubes G and D were sealed off. The apparatus was then continuously evacuated, with the liquid in H_1 frozen with liquid air, and the apparatus strongly heated as before to remove adsorbed gases (avoiding, however, heating the bottom of J_1, etc., because of the mercury bulb). After about 3 hours' evacuation, tap T_2 was closed; the water in H_1 was slowly melted and then distilled from H_1 (at 30—40°) in H_2 (cooled in ice). At the end of this distillation, H_2 was cooled in liquid air, and the apparatus evacuated for some hours. This cycle of operation was repeated twice, after which the outgassed water was distilled *in vacuo* into J_1, which was then sealed at the constriction L. Four separate samples could be prepared simultaneously in this way.

By inclining tube J_1 slightly, the side-tube N could be partially filled with water, and then sealed off. This enabled a check analysis to be carried out on the water, in particular to investigate the presence of mercury (*e.g.*, from diffusion pumps) in the vessel. The mercury bulb was next broken by careful shaking, thereby bringing mercury and water into contact *in vacuo*, and vessel J_1 was immersed in a thermostat-bath. The period of equilibration was 10 days, as prescribed by Pariaud and Archinard [4] who found that equilibrium was reached at room temperature in this period. The solutions were not shaken, since we wished to avoid any possibility of suspended or colloidal mercury in the solution.

Standard Solution.—A standard solution was prepared by dissolving 0·24220 g. of mercuric chloride in 250 ml. of distilled water, then diluting 5 ml. to 100 ml. with dilute sulphuric acid; acid is necessary to present adsorption by the glass,[27] and the only relevant work [28] reports that sulphuric acid contains less mercury as impurity than do the other mineral acids. The final solution contained 48·44 μg./ml.; its density at 25° was $0{\cdot}991_4$ g./ml.

By a technique similar to that described below, 1 drop of freshly prepared solution was transferred to a weighed silica irradiation phial of 4 mm. diameter, and the weight of solution in the phial was determined. Distilled water was then added to dilute the solution in the phial (~10-fold), and to give a depth of solution approximately the same as in the phials containing solution samples. The phial was subsequently sealed and treated in the same way as the solution samples. The dilution of the standard solution was necessary for two purposes. First, attenuation of the neutron flux is reduced, since self-shielding falls off exponentially with decreasing concentration and should be negligible with the diluted solution. Secondly, any differences in the effective neutron flux received by sample and standard, due to inhomogeneity, are minimised by keeping the depth of solution the same in both cases.

Sampling, Packing, and Neutron Bombardment.—Great care was taken to avoid contamination during sampling, especially since laboratory air normally contains appreciable quantities of mercury vapour [28-30] and since mercury is strongly adsorbed on glass.[27] To avoid the first difficulty the thermostat-baths were placed in an office room where chemicals were not handled. The silica irradiation phials were prepared in advance, cleaned as described above, and heated to red heat to drive off adsorbed material, and both ends were then sealed until required. The tubes, and similarly treated silica sampling pipettes, were stored in a desiccator until required.

Immediately before sampling, three phials were opened and a thin silica funnel was inserted in the neck of each to prevent liquid wetting the neck during the filling. The sampling pipette was meanwhile opened and placed in a silica guard-tube heated electrically to a temperature slightly above that of the solution in question. The solution vessel was next raised to be half-immersed in the thermostat-bath and the top was broken off at a previous knife-mark; the sampling pipette was washed through with solution, which was rejected, and an appropriate volume of solution was transferred to the phial, which was cooled in ice. The phial was then quickly sealed. The whole operation needed about 1 minute. The weight of solution was determined later. Two samples were taken from each solution; the third phial contained distilled water to provide a control test of the sampling procedure.

All the sealed phials were tested by heating at 100° for 24 hr., and then packed in the standard aluminium irradiation can. Each can contained 2 pairs of samples and a pair of standards, as well as 2 control tests, with sufficient silica wool to prevent movement. As far as possible, each phial was placed symmetrically in the can with respect to its duplicate. Calculations based on the equation given by Hughes [31] showed that flux depression should be negligible under these conditions.

The solutions were irradiated for approximately 1 week in BEPO at pile factor 12. No phials burst. After transport to the laboratory, the cans were left for 1½ days to " cool "; the phials were then removed, washed extensively with alcohol and water, and finally immersed overnight in aqua regia. The phials were again thoroughly washed with water before chemical treatment.

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[27] Sandell, " Colorimetric Determination of Traces of Metals," 3rd edn., Interscience Publ., Inc., New York, 1959, p. 622.

[28] Stock, Lux, Cucuel, and Köhle, *Z. angew. Chem.*, 1933, **46**, 62.

[29] Stock and Lux, *Z. angew. Chem.*, 1931, **44**, 200.

[30] Ditchburn and Gilmour, *Rev. Mod. Phys.*, 1941, **13**, 210.

[31] Hughes, " Pile Neutron Research," Addison-Wesley, Cambridge, Mass., 1953, p. 86.

Chemical Separation of Radioactive Mercury.—Although γ-ray spectrometry was used in the counting, the presence of " foreign " activities with energies similar to those being detected is always possible. For example, Leliaert[32] has shown that appreciable activities may arise from the impurities present in the silica. Chemical separation of the active mercury was therefore carried out before counting.

The phial (either standard or sample) was first centrifuged to collect all the liquid at the bottom of the tube, and the solution then frozen in liquid air before being broken open. This freezing was necessary because of the considerable pressure (at room temperature) of the gaseous radiolysis products. Both parts of the broken phial were placed in a flask containing inactive mercury carrier (15 mg. for solution, 30—45 mg. for standard) in 3·5M-nitric acid. The phial was completely covered with acid ($\sim$15 ml.) which was forced into any empty spaces with a dropper; all washings were returned to the flask, whose contents were gently refluxed for 1 hour. This treatment completely removed active mercury from the phial, and also ensured that active and carrier mercury had the same chemical form. The broken pieces of the phial were removed, and the washings, and those from the condenser, were added to the flask. Since nitric acid does not attack silica, this treatment should not bring any foreign activities into solution.

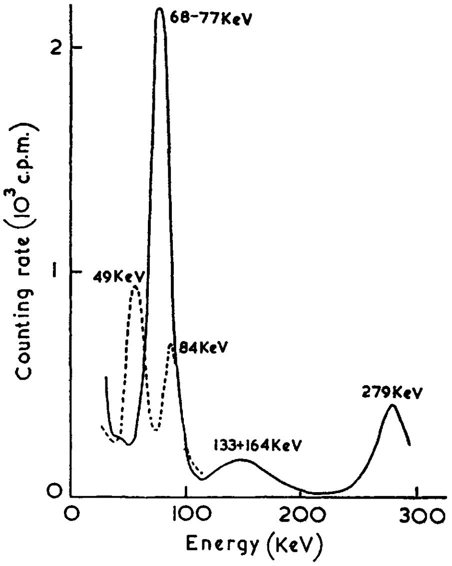

FIG. 3. γ-Ray spectrum of ^{197m} + ^{197}Hg (full line), and of ^{170}Tm (broken line).

Hydrogen sulphide was passed through the solution for about 1 hr., precipitating mercuric sulphide (see Stock *et al.*[28]); the solution was warmed on a water-bath during the early part of this period. Oxidation of the precipitate by nitric acid does not occur if hydrogen sulphide is always present in excess.[28] The precipitate was finally collected by long centrifugation. and washed twice with 2M-hydrochloric acid. The supernatant liquor showed no mercury activity, although a small (unidentified) activity was detected. The precipitate was dissolved in a few drops of aqua regia; 3 ml. of concentrated hydrochloric acid were added to this solution, and the mixture evaporated almost to dryness to remove nitric acid. 2M-Hydrochloric acid (20 ml.) and silver nitrate solution (1 mg. of Ag^+ per ml.; 5 ml.) were added; this silver chloride precipitation " scavenges " out any foreign activities, and also removes any colloidal sulphur present. This scavenging was repeated, and mercuric sulphide then precipitated from the dilute hydrochloric acid solution.

The centrifuged precipitate was washed (twice with dilute hydrochloric acid, twice with water, once with acetone), and the acetone slurry was filtered through a constant-weight glass-wool filter paper (Waterman glass paper, W. and P. Balston Ltd.). Each filter was dried at 105° for 1½ hr. in a separate Petri dish to prevent cross-contamination; in addition, a similar

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[32] Leliaert, *Pure Appl. Chem.*, 1960, **1**, 120.

weight of inactive mercuric sulphide was dried at the same time to check for possible contamination in the drying process. The chemical yield of mercury was obtained from the weight of the dry precipitate. The filter paper and precipitate were mounted on an aluminium counting tray with a few drops of Perspex solution; after this had evaporated, the sample was covered with Sellotape.

γ-Ray Spectrometry.—The counter consisted of a 1″ × 1″ NaI(Tl) crystal and photomultiplier tube coupled *via* a linear amplifier to either a " Philips " single-channel pulse-height analyser, or a 50-channel analyser. The radiochemical purity of each precipitate was checked by recording its γ-ray spectrum in the 30—300 Kev region with the 50-channel analyser, and by comparing this with the spectrum of ^{170}Tm, with photopeaks at 84 (γ) and 49 (*X*-ray) Kev. A typical spectrum (Fig. 3) shows the 68—77 Kev photopeak broadened on the low-energy side; the resolution is ~25%. The Compton scattering from higher-energy radiation is negligible in this region.

The final activity measurement involved counting the pulses in the 68—77 Kev band (indicated in Fig. 3), by using the single-channel analyser. The samples were placed about 0·4 cm. from the front surface of the crystal. At least $1·5 \times 10^4$ counts were recorded for each sample, thus reducing the statistical error to below 1%. This number of counts could be recorded in a time sufficiently short that no decay correction for decay was necessary.

RESULTS AND DISCUSSION

Reliability of the Separation Method.—Two phials containing standard solution (calculated weight of Hg 1·846 and 2·598 μg., respectively) were irradiated, and mercuric sulphide was precipitated in the usual way, except that each solution was subdivided quantitatively before sulphide precipitation to give 3—4 separate counting samples. The activity of each precipitate was determined about 1 week after the end of irradiation. The samples were counted in the order 1—1, 1—2, . . . 2—3, and then in reverse order; the duplicate values for any one sample agreed within statistical error, showing as expected that no short-lived activities were present. The results in Table 3 show that the (mean) counting rate is proportional to the weight of mercury present. The mean value for set (1) is $2·77 \pm 0·01$ (3σ) and for set (2), $2·92 \pm 0·12$. It is worth noting that from these results the activity 65 hours after the end of the irradiation would be $7·5 \times 10^4$ c.p.m./μg., in excellent agreement with the value calculated earlier.

TABLE 3.
Activities of mercuric sulphide precipitates.

Sample	Wt. of HgS ppt. (mg.)	Calculated wt. of irradiated Hg (μg.)	Counting rate (c.p.m.)	10^{-4} c.p.m./μg.
1—1	5·06	0·179	5047	2·82
1—2	8·25	0·292	7847	2·69
1—3	13·25	0·467	12,905	2·76
1—4	21·50	0·761	21,443	2·82
2—1	10·53	0·523	15,621	2·99
2—2	16·55	0·824	23,771	2·89
2—3	21·35	1·063	30,715	2·89

It was found experimentally that the ratio of activities of different samples did not change with time; thus, in a typical example the sample : standard ratio did not vary by more than ±0·5% during 12 days. The amount of mercury in the irradiated solutions could therefore be calculated from such a ratio by normalisation to a standard time.

No activities other than those of isotopes of mercury were found in the final precipitates. No significant mercury activity was found in any of the neutron-irradiated control solutions, or in the inactive mercuric sulphide precipitates dried alongside the active samples.

Solubility Results.—Table 4 gives the final results for the solubility of mercury in water over the range 25—90°. Two experiments were carried out at each temperature (three at 25°), and duplicate samples were taken in each experiment.

The statistical errors were calculated from the standard tables;[33] the values of 3σ

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[33] " Handbook of Chemistry and Physics," 41st edn., Chemical Rubber Publ. Co., 1959, p. 208.

represent 99·6 confidence on the mean, and in general the accuracy is well within that usually obtained in neutron-activation analysis. The results at 90° are more widely spread than the others and we believe that this is due to experimental difficulties in sampling at the surface of a steaming thermostat, since amongst other problems this necessitated much longer sampling times.

TABLE 4.

Solubility of mercury in water.

Temp.	Mean value (10^{-7} g./g.)	Probable error on mean	3σ (%)	Temp.	Mean value (10^{-7} g./g.)	Probable error on mean	3σ (%)
25°	0·631	0·14	10·4	65°	2·17	0·05	9·7
35	1·09	0·03	12·3	80	2·61	0·01	2·5
50	1·77	0·03	8·3	90	3·34	0·18	23·6

The present work represents the first series of results over a range of temperatures, but they can be compared with the various individual results. Stock's value of 2—3 × 10^{-8} g./g. at 30° is appreciably lower than our result, and the same is true of Pariaud and Archinard's results (2—2·5 × 10^{-8} g./g. at 25°, and 2·3—3·2 × 10^{-8} g./g. at 28°). Stock's figure of 3 × 10^{-7} g./g. at 85° is in good agreement with our results, but his value at 100° (6 × 10^{-7} g./g.) is much higher, as is Reichardt and Bonhoeffer's result of 10^{-7} g./ml. at 120°, although pressure effects may account for these differences to some extent. We find excellent agreement with Moser and Voigt's result at 25°, namely, $6{\cdot}0 \pm 0{\cdot}6 \times 10^{-8}$ g./g. Since their radiochemical method is almost certainly more reliable than those used in the older experiments just quoted, and since it involved a very different technique from ours, we believe that this good agreement shows not only that our results give good internal agreement, but also that no serious systematic error had affected them. The solubility shows a smooth temperature-dependence; it is hoped to discuss the implications of this in a later publication.

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