as lead dioxide by dissolving in dil. nitric acid, filtering off any dioxide from the hydrolysis of unchanged lead tetrafluoride, adding alkaline hydroxide in excess and passing chlorine into the suspension of lead hydroxide below 50°. The precipitation of lead dioxide is practically quantitative according to the equation

$$PbO.H_2O + NaClO = PbO_2.H_2O + NaCl.$$

All fluorine remaining in solution may be recovered by precipitating as calcium fluoride which with sulfuric acid will regenerate the hydrofluoric acid used up. The entire recovery process as tested out on an experimental basis is 95% efficient.

Evolution of Fluorine.—The practically pure tripotassium lead hydrogen octafluoride has been used to advantage for the evolution of fluorine. Four hours at 250° usually suffice to drive off the hydrogen fluoride, and evolution of fluorine, as indicated by the formation of iodine crystals on potassium iodide paper, is evident at 300°. No experiments of this sort have been as yet possible with *pure* disodium lead hexafluoride because of the great difficulty in obtaining it pure. In every case the product has been contaminated with sodium hydrogen fluoride from which all the hydrogen fluoride could not be driven at 250°. There were strong indications of fluorine, however, from the salt even at 250°, so that undoubtedly the evolution from the pure salt would begin at quite low temperatures, which would of course be a distinct advantage.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF YALE UNIVERSITY.]

ON THE SULFITE METHOD FOR THE SEPARATION AND DETERMINATION OF GALLIUM WHEN ASSOCIATED WITH ZINC.

BY LYMAN E. PORTER AND PHILIP E. BROWNING.

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The frequent occurrence of gallium with zinc makes the separation of these elements of especial importance. The usual method of separation consists in the precipitation of the gallium hydroxide by ammonium hydroxide in the presence of ammonium salts, the zinc remaining in solution.[1] This method has several disadvantages, for not only is it necessary to boil for a long time to expel the excess ammonia, in order that the precipitation may be complete, but in the process an appreciable amount of the gallium compound, the precipitate, usually adheres to the containing vessel; moreover, when extracting any considerable amount of gallium from material containing zinc, such as the leady residue from the purification of zinc or the gallium-indium alloy obtained from this

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[1] Lecoq de Boisbaudran, *Compt. rend.*, 94, 1625 (1882).

residue,[1] the gelatinous nature of the gallium hydroxide results in slow filtration and a tendency to include a considerable amount of the soluble zinc salts even after several reprecipitations. Various procedures have been suggested to overcome these difficulties. Dennis and Bridgeman[2] precipitate the zinc by the use of potassium mercuric thiocyanate, leaving the gallium in solution; the mercury is then removed by hydrogen sulfide. The gallium is separated by boiling the solution with sodium sulfite in the presence of hydrochloric acid, or by using ammonium sulfite. Care must be taken, the authors state, to have the acid concentration right, otherwise some gallium is dissolved, either by the excess of acid or by the alkali formed by the hydrolysis of the sodium sulfite.

The work described in the present article has to do with a direct application of the sulfite method to the separation of moderate amounts of zinc from gallium. It is assumed that any indium originally present has been previously separated by sodium hydroxide and that the greater part of the zinc has been removed by precipitating the gallium hydroxide in the presence of ammonium chloride.[3,4] The reagents used are sodium hydrogen sulfite and ammonium hydrogen sulfite, formed by saturating, respectively, with sulfur dioxide a 10% solution of sodium sulfite and dil. ammonium hydroxide (1:4).

Preliminary experiments showed that 0.0002 g., or even less, of gallium can be precipitated in 5 cc. of solution by boiling with a drop or two of either of these reagents. Similar experiments on solutions containing zinc showed no precipitation even after boiling 10 minutes, although it may be precipitated from neutral solutions by neutral sodium sulfite. To test the completeness of the gallium precipitation, a study was made of the delicacy of the potassium ferrocyanide test,[5] with a view to using it to detect gallium in the filtrate after the sulfite precipitation. In hydrochloric acid solution as small an amount as 0.0001 g. of gallium in 5 cc. of solution can be detected by the ferrocyanide.[6] It was found, however, that if 0.002 g. of gallium in 5 cc. of solution is treated with ammonium hydrogen sulfite in the cold, no precipitate forms upon the addition of the ferrocyanide, nor does it come down on long standing. The addition of an excess of hydrochloric acid to this solution, however, causes precipitation. By the use of smaller amounts of gallium it was found that the delicacy of the test is not interfered with by the sulfite, provided that sufficient hydrochloric acid or other strong acid is present.

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[1] Browning and Uhler, and Uhler and Browning, *Am. J. Sci.*, **41**, 351 (1916); **42**, 389 (1916).

[2] THIS JOURNAL, 40, 1531 (1918).

[3] Lecoq de Boisbaudran, *Loc. cit.*

[4] Browning and Uhler, *Ibid.*

[5] Lecoq de Boisbaudran, *Compt. rend.*, **99**, 526 (1884).

[6] Browning and Porter, *Am. J. Sci.*, **44**, 221 (1917).

This constitutes a difference between the behavior of gallium and that of zinc, because the latter may be precipitated as the ferrocyanide from a solution containing sulfite, even in the absence of strong acid.

A series of precipitations of gallium was made from neutral or slightly acid solutions by boiling them with ammonium hydrogen sulfite. Amounts of gallium ranging from 0.0005 g. to 0.005 g. calculated as the metal, were used. The filtrates from the precipitations were treated with hydrochloric acid and potassium ferrocyanide. Negative results proved the completeness of the precipitation.

The following procedure for the qualitative detection and separation of gallium and zinc was tried successfully on unknown solutions. The results are given in Table I. The neutral or slightly acid solution, about 5 cc., is boiled for two minutes with sodium hydrogen sulfite. A precipitate, indicating gallium, is filtered off after it settles. Hydrochloric acid is then added to the filtrate, followed by potassium ferrocyanide. A precipitate here shows the presence of zinc. Similar results were obtained by substituting ammonium hydrogen sulfite for the sodium salt. In the table, Expts. 11 to 13 are significant in that the failure to get a test with the ferrocyanide gives additional evidence that the precipitation of gallium is complete.

TABLE I.

Qualitative Detection of Gallium and Zinc.

Expt.	Taken G.	Found.	
1	Ga 0.0001	Ga present (doubtful)	Zn absent
2	Ga 0.0002, Zn 0.0015	Ga present	Zn present
3	Zn 0.001	Ga absent	Zn present
4	Ga 0.0002, Zn 0.0003	Ga present	Zn present
5	Ga 0.0003	Ga present	Zn absent
6	Zn 0.0002	Ga absent	Zn present
7	Ga 0.0002	Ga present	Zn absent
8	Zn 0.0005	Ga absent	Zn present
9	Distilled water	Ga absent	Zn absent
10	Ga 0.0003	Ga present	Zn absent
11	Ga 0.005	Ga present	Zn absent
12	Ga 0.0025	Ga present	Zn absent
13	Ga 0.005	Ga present	Zn absent

This method lends itself well also to the quantitative estimation of gallium in the presence of zinc, on account of the granular form of the precipitate. The gallium is conveniently precipitated from 200 cc. of solution, which is neutral or slightly acid. After the addition of 4 or 5 cc. of ammonium hydrogen sulfite the solution is heated to boiling for from 3 to 5 minutes. At the end of this time the precipitate of gallium is in distinctly granular form and settles readily. The supernatant liquid is decanted through a filter paper. The precipitate left in the beaker is dissolved by the addition of a few drops of hydrochloric acid and 200 cc.

of water is added. The gallium is reprecipitated as before, and the precipitate is filtered off upon the original filter paper, ignited, and weighed as Ga_2O_3. It was found that if the gallium is not reprecipitated when zinc is present a somewhat high result is obtained, but this is obviated by a single reprecipitation.

Expts. 9 and 10, Table II, are of special interest, because in the former the gallium was reprecipitated 3 times, and in the latter twice, the results showing that this precedure does not result in any loss of gallium.

TABLE II.

Quantitative Estimation of Gallium Precipitated by Ammonium Acid Sulfite.

Expt.	Amount $ZnCl_2$ taken. G.	Amount Ga_2O_3 taken. G.	Amount Ga_2O_3 found. G.	Error. G.
1	0	0.0202	0.0203	0.0001 +
2	0	0.0236	0.0235	0.0001 —
3	0.1	0.0202	0.0199	0.0003 —
4	0.1	0.0202	0.0203	0.0001 +
5	0.35	0.0151	0.0149	0.0002 —
6	0.3	0.0202	0.0201	0.0001 —
7	0.1	0.0236	0.0236	0.0000 ±
8	0.1	0.0236	0.0239	0.0003 +
9	0	0.0472	0.0471	0.0001 —
10	0	0.0236	0.0234	0.0002 —

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[CONTRIBUTION FROM THE DEPARTMENT OF NUTRITION, OHIO AGRICULTURAL EXPERIMENT STATION.]

THE MODIFIED BENEDICT METHOD FOR THE ESTIMATION OF SULFUR IN FEEDS, FECES AND FOODS.[1]

BY J. O. HALVERSON.

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In the estimation of total sulfur in solid organic matter, the Wolf and Osterberg procedure[2] of adding fuming nitric acid in the preliminary oxidation and solution of the material (before final and complete oxidation with the Benedict reagent[3]) offers two great difficulties which prevent its general availability for those classes of substances for which the official peroxide method[4] is applicable. First, the use of large amounts (50 to 75 cc.) of fuming nitric acid in Kjeldahl flasks heated over a free flame is tedious, long, and effect solution with difficulty. Second, the

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[1] An abstract of the work included in this paper was presented at the Cleveland meeting of the American Chemical Society, Sept. 12, 1918.

[2] *Biochem. Z.*, **29**, 428 (1910).

[3] The Benedict reagent consists of 200 g. of crystallized copper nitrate, sulfur-free or of known sulfur content; 50 g. of potassium or sodium chlorate and distilled water to make 1000 cc.

[4] Report of the Committee on Editing Tentative and Official Methods of Analysis of the Association of Official Agricultural Chemists, 1915, p. 32.