be interpreted as such. However, the complexity of the hydrogen sulfide spectrum beyond 4μ tends to make this comparison uncertain.

Summary

1. The infra-red absorption spectra of several alkyl and aryl mercaptans and sulfides have been examined with a recording quartz spectrograph.

2. A single band at 1.99–2.00μ differentiates the spectrum of a mercaptan from the corresponding sulfide. This band is regarded as the first harmonic of one found by Bell at 3.8–3.9μ, and both are interpreted as originating in the S–H bond.

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GALLIUM. III. QUANTITATIVE SEPARATION OF IRON FROM GALLIUM BY MEANS OF ALPHA-NITROSO-BETA-NAPHTHOL[1]

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The method frequently employed for separating iron from gallium is based on the property of trivalent iron to form a precipitate on the addition of an excess of fixed alkali hydroxide while gallium, being amphoteric, passes into solution as alkali gallate. This method was first used by de Boisbaudran,[2] the discoverer of gallium, and in so far as the preparation of iron-free gallium is concerned it will be found satisfactory; the resulting alkali gallate and the gallium hydroxide and oxide ultimately obtained from it will be found on spectroscopic examination to contain negligible traces of iron, provided care is taken to prevent contamination through reagents and containers. A similar examination of the residual ferric hydroxide will reveal that even after thorough washing, small quantities of gallium are retained. This can be undoubtedly ascribed to the strong adsorptive power of ferric hydroxide, a phenomenon frequently observed in similar cases.

In extracting gallium from a natural mineral or in recovering it from commercial products, iron which is always present will accompany the

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[2] De Boisbaudran, *Compt. rend.*, **94**, 1439, 1625 (1882).

gallium through the various stages of concentration. Furthermore, in the separation of gallium from aluminum by converting the former to the ferrocyanide, large quantities of iron are unavoidably introduced in the form of the precipitating agent. It may be worth while to remark in passing that the ferrocyanide method is among the best for separating gallium from aluminum.[3] In either case the chemist is confronted with the necessity of separating iron from the gallium. Papish and Holt[4] employed α-nitroso-β-naphthol for this purpose. An examination of the residual iron salt obtained by this method proved that it was free, even in a spectroscopic sense, from gallium. This at once suggested itself as a suitable method for quantitative analytical work and the following experiments were undertaken to determine its applicability.

A solution of α-nitroso-β-naphthol was prepared by dissolving 1 g. of the reagent in 50 cc. of a 50% solution of acetic acid. It was made up fresh and filtered each time before using.

A solution of ferric chloride of known concentration was prepared by dissolving the salt in a definite volume of water and determining the iron content as ferric oxide by adding ammonium hydroxide to a small portion of the solution and washing, igniting and weighing the precipitate. The ferric chloride, before being dissolved, was examined spectroscopically for gallium and aluminum and was found to be free from both these elements.

Ignited gallium oxide, which on spectroscopic examination was proved to be free from iron,[5] was dissolved in hot aqua regia, boiled with separate portions of hydrochloric acid and the resulting solution of gallium trichloride, freed from the oxides of nitrogen, was diluted with water to a definite volume. The gallium content of this solution was determined in duplicate samples as follows. Two 20cc. portions were transferred to beakers and an excess of ammonium hydroxide was added to each. The solutions were boiled until a moistened piece of red litmus paper did not turn blue on exposure to the vapors evolved from them. On cooling, the precipitates of gallium hydroxide were collected on ashless filter papers and washed with a dilute solution (about 1%) of ammonium nitrate until washings gave no test for chlorides.

If it was noticed or even suspected that some gallium hydroxide adhered to the walls of the beaker, a small amount of hydrochloric acid was added and the gallium was reprecipitated with ammonium hydroxide in the manner just described. While this additional precipitate could have been added to the bulk of gallium hydroxide on the filter, it was found more expedient to collect and wash it on a separate filter paper. The tendency of precipitated gallium hydroxide to adhere to the walls of the container is to be taken into consideration while working with this substance.[6] This tendency is pronounced when the concentration of gallium

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[3] For details of this method see Crookes' "Select Methods in Chemical Analysis," 3d ed., Longmans, Green and Co., London, **1894**, p. 159.

[4] Papish and Holt, *J. Phys. Chem.*, **32**, 142 (1928).

[5] As a matter of fact the small amount of iron was removed from this sample of gallium oxide by a previous treatment with α-nitroso-β-naphthol.

[6] See Dennis and Bridgman, THIS JOURNAL, **40**, 1545 (1918).

is high and when the boiling is prolonged, and it becomes negligible in the case of small quantities boiled for a short time.

The filter papers and contents were transferred to previously weighed porcelain crucibles and ignited to constant weight. Freshly ignited gallium oxide is quite hygroscopic and in order to prevent errors from this source the crucible containing the oxide was placed in a stoppered weighing bottle after ignition, allowed to cool in a desiccator and weighed with the bottle.

Measured volumes of solutions of iron chloride and of gallium chloride, each of known concentration, were mixed, and to the mixture ammonium hydroxide was added carefully until a slight, permanent precipitate resulted which dissolved on the addition of a drop of hydrochloric acid. One or two additional drops of hydrochloric acid were added to insure acid reaction and an excess of a 50% solution of acetic acid was added. A very good alternate method consists in using ammonium acetate in place of acetic acid. This will insure the absence of hydrochloric acid as such, though a very small amount of this acid works no hardship with the procedure. The reagent α-nitroso-β-naphthol in acetic acid was next added to insure excess and the whole was allowed to stand for several hours. The precipitated ferric α-nitroso-β-naphtholate was removed by filtration, washed, first with a 50% solution of cold acetic acid and then with water. After drying, the filter paper and contents were transferred to a porcelain crucible and ignited to constant weight over a Mėker flame. This ignition must be carried out very carefully so as to prevent mechanical loss which will be caused by too rapid decomposition of the organic compound.[7] The iron was weighed as ferric oxide.

The galliferous filtrate from the ferric α-nitroso-β-naphtholate was evaporated to dryness to expel the acetic acid and ammonium hydroxide was

TABLE I

SEPARATION OF IRON FROM GALLIUM

Sample no.	Wt. of Fe_2O_3 taken, g.	Wt. of Ga_2O_3 taken, g.	Wt. of Fe_2O_3 found, g.
1	0.0044	0.0515	0.0044
2	.0222	.0257	.0221
3	.0443	.0515	.0443

TABLE II

DETERMINATION OF IRON AND GALLIUM

Sample, no.	Wt. of Fe_2O_3 taken, g.	Wt. of Ga_2O_3 taken, g.	Wt. of Fe_2O_3 found, g.	Wt. of Ga_2O_3 found, g.
1	0.0425	0.0394	0.0420	0.0394
2	.0425	.0394	.0421	.0399
3	.0425	.0394	.0428	.0391
4	.0222	.0515	.0223	.0515

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[7] It was not found necessary to add oxalic acid to the ferric α-nitroso-β-naphthalate before ignition as suggested by Illinski and Knorre in connection with the separation of iron from aluminum, see *Ber.*, **18**, 2728 (1885).

added to distinct alkalinity. From this point on the procedure was identical with the one already described in connection with the determination of gallium in the original solution of gallium chloride. The results are recorded in Tables I and II.

At the completion of the determinations the oxides of iron and gallium were examined spectroscopically[8] with the following results. The oxides of iron, as already mentioned, were invariably found to be free from gallium. The oxides of gallium contained negligible quantities of iron, a fact established by the presence only of the more persistent spectral lines of this element, λλ 2382.0, 2395.6, 2596.4 and 2599.4 Å.

Summary

A quantitative method is described for the separation of iron from gallium by means of α-nitroso-β-naphthol.

It is proved spectroscopically that the iron separated by this method is free from gallium.

It is proved spectroscopically that the gallium obtained from such a separation contains negligible traces of iron.

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF THE MOORMAN MFG. CO.]

AN ACCURATE METHOD FOR THE DETERMINATION OF IODINE IN MINERAL MIXTURES[1]

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The addition of potassium or calcium iodide to mineral mixtures to be fed to farm animals has made necessary the accurate estimation of iodine in such mixtures, both by the manufacturer and by the feed control chemist. The volatility of iodine under certain conditions, its probable adsorption upon the charcoal which is commonly found in such mixtures and the very small amounts which are permissible, tend to complicate the situation.

Simple extraction methods, using water, alcohol or alkali, were tried by the authors and found to be entirely inadequate. Except in freshly prepared mixtures, less than half of the iodine was recovered by extraction. Using samples of mixtures containing charcoal, it was found that the sum of the iodine in the alcoholic extract and in the residue approximated the total amount present, 40 to 50% of this amount being found in the extract.

Combustion of the sample in a silica tube and determination of the iodine by the method of McClendon[2] or by a combination of this method with

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[8] See Papish and Holt, ref. 4, for the arc spectrographic method employed.

[1] Presented at the St. Louis meeting of the American Chemical Society, April 18, 1928.

[2] McClendon, *J. Biol. Chem.*, **60**, 289–299 (1924).