

notably in a Missouri sulfide, the very rare element germanium. These observations concerning germanium are of particular interest to us since in recent work we also have encountered this element in a by-product derived from Wisconsin blende. The exact nature of this by-product it is not possible to disclose at present.

The occurrence of germanium in blendes has been noted by Urbain.¹ By spectroscopic methods this investigator detected germanium in thirty-eight out of eighty-four blendes from various localities. From five hundred and fifty kilos of one of the richest of these, a Mexican blende, he obtained five grams of pure germanium. The amounts of the element found have always been small, the aid of the spectroscope being usually required to establish the identification. In the material at our disposal, however, germanium was found in sufficient quantity to be readily detected by the ordinary chemical reagents.

The presence of an unusual element had been indicated in the course of analysis and further investigation showed that this was some member of the tin sub-group of the hydrogen sulfide group. The materials were therefore examined for the less common elements of this group. By the experiments briefly outlined in the succeeding paragraphs we convinced ourselves that we were dealing with an altogether unsuspected constituent, the element germanium, and that it was present in considerable amount.

Several one hundred-gram portions of the substance were treated with concentrated hydrochloric acid and the resulting solutions were distilled to about one-half volume, a current of chlorine being passed through the boiling mixture to maintain the arsenic in the pentavalent form. The distillate contained the unknown element.

On dilution of the distillate with a small amount of water and treatment with hydrogen sulfide a white flocculent precipitate was formed. If, however, the distillate was greatly diluted with water such precipitation took place but slowly and incompletely; the addition of strong hydrochloric acid to such solutions caused immediate precipitation. A considerable excess of strong acid was always found necessary for rapid precipitation of the sulfide.

The white sulfide, precipitated from strongly acid solutions, was somewhat soluble in water. It was readily soluble in ammonia and in alkaline sulfide solution. The sulfide yielded on ignition a white residue, soluble in water and in ammonia.

To an aqueous solution of the sulfide a little hydrofluoric acid was added and the solution saturated with solid potassium chloride. A heavy grayish white gelatinous precipitate resulted.

These reactions agree throughout with the properties ascribed to germanium by Winkler. The boiling point of the tetrachloride of germanium is 86°. The sulfide of germanium is white. It is soluble in water and in alkali and is precipitated only from strongly acid solutions. The formation of a double potassium fluoride is particularly characteristic.

¹ *Compt. rend.*, 149, 602; 150, 1758.

From two portions of a solution of germanium sulfide in water the sulfide was precipitated with strong acid and hydrogen sulfide. The sulfide was filtered on a Gooch, dried at 110° and weighed. It was then dissolved in ammonia and the crucibles reweighed. The ammoniacal solutions were evaporated to dryness in platinum and the residues transformed to oxides by the method recommended by Winkler. The results follow.

Determination No.	1	2
Weight of sulfide.....	0.0820	0.0812
Weight of oxide.....	0.0614	0.0604
Ratio oxide/sulfide.....	0.749	0.744

The theoretical ratio $\frac{\text{GeO}_2}{\text{GeS}_2}$ is 0.766, assuming the value 72.5 for the atomic weight of germanium.

A roughly quantitative determination of the amount of germanium present in the material was carried out as follows: After distillation with hydrochloric acid and chlorine the sulfide was precipitated from the distillate with hydrogen sulfide. In some experiments the sulfide was weighed directly; in others it was transformed into oxide with nitric acid and weighed as GeO_2 . The mean of several closely agreeing determinations gave the value $\text{GeO}_2 = 0.25$ per cent.

To show whether or not germanium could be found in other zinc ores, samples of similar by-products from different ores were distilled with hydrochloric acid and chlorine. The distillates, after dilution, were treated with hydrogen sulfide. If no precipitate was obtained the test was considered negative. If a precipitate was obtained (other than the turbidity of sulfur) it was filtered off and transformed to oxide with nitric acid. The final test consisted in the formation from the residue of the double potassium fluoride with hydrofluoric acid and potassium chloride.

From several of the materials very definite confirmatory tests were obtained; others gave satisfactory blanks, while in only a few instances were the results uncertain. In none of the cases where positive results were secured was there found an amount of germanium at all comparable to that found in the material first examined, probably not one-tenth as much. A positive test was secured from Joplin ore and also from some Mexican ores. The Franklin ores gave negative results.

The germanium oxide prepared as described above has been examined spectroscopically by Dr. Burns, of the Bureau of Standards, who reports as follows: "It shows: zinc, *absent*; lead, *weak*; silicon, *present*; tin, *fairly strong*; copper, *present* (possibly the last three were introduced accidentally by us); cadmium, *trace*; germanium, *principal constituent*; gallium, *present*; indium, *trace*."

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SODIUM SULFATE AS A SUBSTITUTE FOR POTASSIUM SULFATE IN THE GUNNING MODIFICATIONS FOR DETERMINING NITROGEN

By W. L. LATSHAW

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Owing to the extremely high price of potassium sulfate, chemists who favor the Gunning modification

of the Kjeldahl method for determining nitrogen are looking for a cheaper substitute to take the place of the more expensive potassium sulfate. Quotations recently received at this laboratory from several firms range in price from \$1.25 to \$2.25 per lb. for the powdered chemical suitable for use in nitrogen work, while quotations on suitable sodium sulfate were only 15 c. per lb. Because of the similarity in chemical characteristics between potassium sulfate and sodium sulfate, a series of determinations was made to compare the use of these two salts in making nitrogen determinations.

In the first trials, where 10 g. of the water-free salts were used in comparison, both worked very nicely during digestion, but on cooling, the digest in which sodium sulfate was used caked into a solid mass, and as this was objectionable 7 to 8 g. of sodium sulfate were used with the results shown in Table I.

As nitrogen determinations must be made on materials differing widely in nitrogen content, it was thought well to use such a variety as one might ordinarily be called upon to analyze in every-day work. For this reason the ten different samples listed in the table were used in these determinations.

TABLE I
(RESULTS IN PERCENTAGES)
THE GUNNING COPPER METHOD THE OFFICIAL
SUBSTITUTING GUNNING COPPER METHOD

SUBSTANCES	No. of Dets.			Av.	No. of Dets.	No. of Dets.			Av.
	Max.	Min.				Max.	Min.		
Dried blood...	3	14.97	14.93	14.95	3	14.96	14.92		14.95
Casein.....	3	12.72	12.68	12.70	3	12.71	12.67		12.69
Milk albumin..	6	9.07	8.89	8.99	3	9.00	8.96		8.98
Fertilizer.....	3	3.51	3.46	3.49	3	3.51	3.49		3.50
Alfalfa leaves..	5	3.78	3.61	3.71	3	3.80	3.73		3.77
Alfalfa stems..	3	1.63	1.55	1.59	3	1.63	1.59		1.62
Cob chop.....	3	1.36	1.32	1.35	3	1.38	1.35		1.37
Bone meal.....	3	0.96	0.92	0.94	3	0.94	0.90		0.93
Skim milk.....	3	0.53	0.50	0.52	3	0.53	0.51		0.52
Soil.....	4	0.043	0.038	0.041	3	0.041	0.037		0.039

The figures in the table explain themselves, and as these ten samples include compounds of the highest to the lowest nitrogen content, the writer feels confident in saying that he believes sodium sulfate can be used instead of potassium sulfate when determining nitrogen in any kind of material. The analyses were carried out under exactly duplicate conditions. The period of digestion was 2 hrs. after the solution cleared.

Sodium sulfate, when used in the amounts mentioned, did not in any way prove objectionable in this work. It proved itself just as good an oxidizing agent as potassium sulfate and as it has a higher boiling point, it would be expected to be even better than potassium sulfate. The writer does not maintain that sodium sulfate is preferable to potassium sulfate in nitrogen determinations. There are cases where caking will take place, although this can readily be avoided by diluting as soon as cool. As far as chemical efficiency is concerned, the two chemicals compare very favorably. Where a large number of nitrogen determinations are being made and potassium sulfate is ordered in 50 and 100 lb. lots, a great saving will be realized by using sodium sulfate; as much as \$60 can be saved on one order of 50 lbs.

It should be mentioned here that we have found it more convenient and inexpensive to use copper wire instead of copper sulfate. As is known,¹ the use of

copper sulfate has been adopted officially for use in nitrogen determinations. Its good points have previously been discussed¹ and need no further elaboration. Pieces of copper wire approximating 0.1 g. can readily be cut with a wire cutter.

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SOME DATA ON THE OXIDATION OF AUTOMOBILE CYLINDER OILS

By C. E. WATERS²

Received April 1, 1916

INTRODUCTION

It has long been known that mineral oils become oxidized when subjected to the combined action of sunlight and air. The literature of the subject was rather fully reviewed in a paper published some time ago.³

The so-called "carbonization" of automobile cylinder oils is due, to only a very limited extent if at all, to cracking, but is caused by oxidation⁴ and subsequent polymerization. In order to learn whether there is any close connection between the rate of oxidation of different oils on exposure to light and air, and their carbonization values at elevated temperatures, both before and after oxidation in the light, an extended series of tests was made with three automobile cylinder oils of well known brands. Certain other constants were also determined. As supplemental to the above, the influence of the time and temperature of heating upon the carbonization value was also studied.

A sufficient supply of each of the oils was purchased in the open market. In order to remove adventitious particles of iron rust or other material that might affect the carbonization values and possibly other determinations,⁵ the samples were filtered directly into clean cans. One-liter portions were kept for convenience in dark brown bottles.

The flash and fire points were as follows, the determinations being made in the Pensky-Martens closed cup apparatus:

Oil No.	1	2	3
Flash point.....	215°	210°	205°
Fire point.....	270°	260°	250°

OXIDATION IN SUNLIGHT

In the earlier paper on this subject⁶ it was shown that when an oil is oxidized in the sunlight some water and carbon dioxide are given off. The oil becomes highly acid and an insoluble oxidation product is thrown down, sometimes after only a few hours' insolation. In order to follow the changes in weight of the oils under investigation, seven 10-g. portions of each were placed in 150-cc. Erlenmeyer flasks, the mouths of which were covered with filter paper

¹ A. J. Patten, *Journal A. O. A. C.*, **1**, No. 3, pp. 394-395; O. F. Jensen, *This Journal*, **7** (1915), 38-39.

² Published by permission of the Director of the Bureau of Standards. The complete paper has just appeared as *Technologic Paper 73* of the Bureau of Standards.

³ Bureau of Standards, *Bull.* **7** (1910), 227-234; *This Journal*, **2** (1910), 451-4.

⁴ Bureau of Standards, *Bull.* **7** (1910), 372, 375; Bureau of Standards, *Technologic Paper 4* (1911), 11; *This Journal*, **3** (1911), 236, 237, 815.

⁵ Bureau of Standards, *Technologic Paper 4* (1911), 10, 13; *This Journal*, **3** (1911), 815.

⁶ Bureau of Standards, *Bull.* **7** (1910), 232; *This Journal*, **2** (1910), 453.

¹ *Journal A. O. A. C.*, **1**, No. 4, Part II, 18-21-23.