read until they have died out. It will be noticed that the relation between C and $p\sqrt{M}$ is not strictly linear, even in this range.

The fact that the quartz-fiber manometer reads in terms of $p\sqrt{M}$ rather than p alone of course limits its applicability to those cases in which the gas to be measured has a known molecular weight, or is a mixture in known proportions of gases of known molecular weights. On the other hand, if M is unknown it can be determined by comparing the quartz-gage readings with those of some other form of delicate manometer, such as Carver's, which reads p directly. Evidently, this would furnish a method for identifying an unknown gas, analyzing a mixture of known gases of different molecular weights, and investigating the possibility of dissociation, at very low pressures. The method could be extended to higher pressures, in the first two cases, by reversing the principle of the McLeod gage; that is, by *expanding* the unknown gas in a sufficiently large ratio to bring it within the optimum range of the quartz-fiber gage.

Summary

A form of bifilar quartz-fiber manometer is described, from which troublesome harmonic vibrations are eliminated.

A method is described by which the instrument may be read up to pressures of 0.1 to 1 mm., depending on the gas used. The method involves calibration over the whole range with a permanent gas and a McLeod gage and, in addition, either a single measurement with the gas used and a McLeod gage at relatively high pressure, or a knowledge of the viscosity of the gas. So extended, the range of the instrument overlaps that of the McLeod gage, even with easily condensable vapors.

It is suggested that the gage may be used to determine molecular weights of gases at very low pressures.

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ERRORS IN THE DETERMINATION OF HYDROGEN SULFIDE

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Considerable interest is attached to a knowledge of the quantity of hydrogen sulfide present in natural waters. Such data are of value to the chemist, biologist and the public health officer. Hydrogen sulfide in natural waters is thought to be derived from both organic and inorganic sources and the quantity of it present in any water is likely to undergo rapid and rather great changes. Hydrogen sulfide in solution is rapidly oxidized and careful tests on solutions of the gas in distilled water show that 50% of the hydrogen sulfide may be lost in this way while a solution is kept overnight in a closed container at room temperature. Consequently, the necessity for working with freshly obtained samples of natural waters is evident.

The investigations summarized in this article are the result of experimental work carried on for two summers at the North Dakota Biological Station at Devil's Lake, N. D. Further experiments were conducted at the University of Washington.

Natural waters of the lake region of North Dakota are typical saline waters of such a kind as will cause serious errors in the iodimetric determination of hydrogen sulfide. These lake waters are quite saline and are rich in alkali sulfates and carbonates. They contain considerable magnesium bicarbonate and some calcium bicarbonate. Total solids vary from 12000 to 25000 parts per million. In some instances the sulfate content of the water was more than half of the content of total solids. There appeared to be a slow bacterial reduction of sulfate to sulfide which caused a gradual precipitation of iron as iron sulfide. In many instances samples of mud from the lake bottom evolved considerable hydrogen sulfide upon treatment with hydrochloric acid. Analyses of such mud frequently showed a content of 10% to 12% of iron.

Waters of this lake region contain moderate amounts of ammonia and nitrates. Nitrites are generally absent during summer months.

Methods Now Used for Determination of Hydrogen Sulfide in Water.—In one colorimetric method[1] a lead salt precipitates brown lead sulfide or gives a brown color, the depth of which is dependent upon the amount of sulfide present. The color thus obtained is matched against that of lead sulfide derived from a known quantity of lead salt, and in this way the amount of hydrogen sulfide is measured. Waters rich in chlorides, sulfates or carbonates are not well adapted to the use of this method, since the chloride, sulfate and carbonate of lead are insoluble salts and would precipitate.

The iodimetric method for the determination of hydrogen sulfide is based upon the chemical changes which are illustrated by the following equations: $H_2S + I_2 = 2HI + S$; and $I_2 + 2\ Na_2S_2O_3 = Na_2S_4O_6 + 2\ NaI$.

To a measured quantity of the water is added a known excess of a standard solution of iodine. After a short time the excess of iodine is determined by titration with a standard solution of sodium thiosulfate. The hydriodic acid remains in the solution, and at the high dilution existing the free sulfur is in the colloidal form and does not precipitate. The iodine used is taken as a measure of the amount of hydrogen sulfide present. This process assumes that there is no substance present, other than hydrogen sulfide, which is capable of reacting with iodine. Such a condition does not exist except in very pure waters.

Effect of Organic Matter

Organic matter in general, either animal or vegetable, reacts with iodine and would therefore have a tendency to show a content of hydrogen sulfide somewhat greater than the true value.

Effect of Alkalinity

It is well known that the halogens react readily with hydroxides and carbonates. In iodimetry the presence of alkaline hydroxides or carbon-

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[1] Winkler, *Z. anal. Chem.*, **52,** 641 (1913).

ates must be avoided, because of the reaction between these substances and iodine. Bicarbonates do no harm since they do not react with iodine.

In natural waters we often find carbonate and bicarbonate alkalinity. The former would cause absorption of iodine and consequently the amount of hydrogen sulfide as determined would be higher than the true value. The magnitude of this effect as tested upon natural waters of an average alkalinity is shown in Table I. The alkalinity of the water sample was determined by titration of a separate sample of water.

TABLE I

EFFECT OF CARBONATE ALKALINITY OF WATERS ON IODIMETRIC DETERMINATION OF HYDROGEN SULFIDE

	Parts per million of hydrogen sulfide as measured by iodine absorbed					
Before neutralization..........	2.0	3.5	4.9	6.1	6.7	7.5
After neutralization............	none	0.2	0.06	0.2	none	0.6

These samples were from different sources and their alkalinity varied somewhat, but each sample was carefully neutralized before making the tests recorded in the second line. The errors due to carbonate alkalinity are evident.

Effect of Nitrates

In order to test the effect of nitrates a solution of hydrogen sulfide was prepared in purified distilled water, and the concentration determined by the iodimetric method, using 0.01 *N* solutions of iodine and sodium thiosulfate. To guard against changes in concentration of the hydrogen sulfide solution, because of oxidation, all tests were made immediately after the standardization of the solution. Measured portions of a dilute standard solution of potassium nitrate were then added to known volumes of the solution of hydrogen sulfide, followed by an iodimetric determination of the latter substance in the usual way. Results are given in Table II.

TABLE II

EFFECT OF NITRATE UPON THE IODIMETRIC DETERMINATION OF HYDROGEN SULFIDE

Quantity of nitrogen added as KNO_3 G.	Volume of the solution Cc.	Parts per million of hydrogen sulfide Present	Found by titration	Quantity of nitrogen added as KNO_3 G.	Volume of the solution Cc.	Parts per million of hydrogen sulfide Present	Found by titration
0.004	150	76.0	71.0	0.004	200	5.87	3.0
.004	150	76.0	70.7	.008	200	5.87	1.9
.012	150	76.0	67.0	.002	200	0.70	0.56
.004	200	5.87	2.8	.006	200	0.70	0.50

From these results it is evident that the presence of nitrates causes the titration process to give values for hydrogen sulfide which are distinctly too low. Similar tests show that sodium nitrate acts like potassium nitrate. The explanation of this effect must be either that there is a loss of hydrogen sulfide or that iodine is liberated by chemical reaction in the course of the determination. It was found that nitrate in concentrations similar to those which occur in natural waters, does not oxidize the hydriodic acid formed, at least within any reasonable time, and further search for the cause of the low results was fruitless.

Effect of Nitrites

In order to test the action of nitrites a procedure was followed similar to that used in testing the effect of nitrates. A solution of hydrogen sulfide in pure water was prepared and standardized by the iodimetric method. To portions of this solution of the gas were added known quantities of freshly prepared standard solutions of nitrite, after which the iodimetric procedure was followed as usual. Results of such tests are given in Table III.

TABLE III

EFFECT OF NITRITE UPON THE IODIMETRIC DETERMINATION OF HYDROGEN SULFIDE

Quantity of nitrogen added as sodium nitrite G.	Volume of the solution Cc.	Parts per million of hydrogen sulfide		Quantity of nitrogen added as potassium nitrite G.	Volume of the solution Cc.	Parts per million of hydrogen sulfide	
		Present	Found by titration			Present	Found by titration
0.003	250	9.84	10.12	0.004	120	76.00	87.3
.004	250	9.44	10.00	.004	120	76.00	85.6
.012	250	9.24	10.00	.004	120	76.00	90.7
.021	250	8.64	9.92	.008	120	76.00	88.5
.030	250	8.04	9.92	.004	200	5.87	8.9
.018	250	6.40	7.20	.004	200	5.87	9.2
.024	250	6.40	7.40	.008	200	5.87	11.5
.030	250	6.20	7.68				

The presence of nitrites evidently causes high results in the iodimetric determination of hydrogen sulfide. In other words there is less free iodine in the solution to be titrated by sodium thiosulfate than should be there for the content of hydrogen sulfide known to be present. In order to interpret these results it will be necessary to account for some chemical changes which use up excess of iodine, due perhaps to a product formed by the action of hydrogen sulfide on a nitrite.

The chemical changes shown by the following equations appear as possibilities in connection with the explanation of the results of experiment.

$$2\ HNO_2 + 2\ HI = 2\ H_2O + 2\ NO + I_2 \quad (1)$$

$$I_2 + NaNO_2 + H_2O = NaNO_3 + 2\ HI \quad (2)$$

$$2\ NO + I_2 = 2\ NOI \quad (3)$$

$$NaNO_2 + 3\ H_2S = NaOH + NH_4OH + 3\ S \quad (4)$$

Equation 1 shows liberation of iodine and this does occur in concd. solutions of iodide and nitrite upon acidification. It represents the determination of iodides in presence of other halides. However, this action is contrary to the fact that small amounts of nitrite in very dilute solutions cause too high results in the determination of hydrogen sulfide.

Equation 2 expresses the oxidation of nitrite to nitrate by iodine in dilute solution. Colorimetric tests for nitrate mixed with small amounts of iodine and nitrite in very dilute solutions do not seem to show any appreciable formation of nitrate.

Equation 3 calls for the formation of the compound nitrosyl iodide, NOI. Since nitrosyl bromide is a very unstable substance, even at low temperatures, it is very unlikely that nitrosyl iodide could be formed.

The chemical process illustrated by Equation 4 has been patented[2] for use in connection with the Le Blanc soda process. That this is the reaction which probably takes place has been shown by passing hydrogen sulfide into a very dilute solution of sodium nitrite, acidifying with sulfuric acid, boiling off the hydrogen sulfide and testing for ammonia by the Nessler method. Positive results were obtained. All of the solutions and reagents used were tested, and found to be ammonia free. Both sodium and ammonium hydroxides will use up iodine. Ammonium hydroxide and iodine may also form nitrogen iodide.

Effect of Soluble Iodide

It was thought best to attempt the iodimetric determination of hydrogen sulfide in the absence of any alkali metal iodide, so as to eliminate any possible interference by potassium iodide. For this purpose a standard dilute solution of iodine dissolved in water was titrated; the end-point was less distinct than usual, due to the absence of iodide. As in the previous instances, it was found that nitrites cause high results, while nitrates cause low results.

In further tests it was found that sodium chloride, calcium chloride, magnesium chloride and urea had no effect upon the accuracy of the determination.

Summary

In view of the very evident errors caused by the presence of small quantities of salts the authors recommend that use of the iodimetric process for the determination of hydrogen sulfide in natural water be discontinued. In order to eliminate errors due to the action of nitrites, nitrates and alkali salts we suggest that natural waters be tested for hydrogen sulfide by the colorimetric method of W. Mecklenburg and F. Rosenkränzer in which methylene blue is formed.[3] The need of a qualitative as well as a quantitative method is further shown by the fact that some of the samples from Devil's Lake gave no test by this latter method, but positive results were obtained by the iodimetric method.

SEATTLE, WASHINGTON

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[2] Görlich and Wichmann, *Ger. pat.*, 87,135; *Ber.*, **39**, 606 (1896).

[3] Mecklenburg and Rosenkränzer, through *C. A.*, **8**, 1938 (1914).