Determination of Hydrogen Sulfide (H_2S) in Environment by Indirect Atomic Absorption Spectroscopy

by ANASTASSIOS KOVATSIS and MATTHEOS TSOUGAS
Chair of Chemical and Industrial Toxicology
and Department of Legal Medicine-Toxicology
Aristotelian University of Thessaloniki-Greece

Although H_2S is usually present in the community atmosphere in the parts per hundred million or lower concentration range,it can create an odor nuisance at 0,10 ppm or less.On the other hand this gas exhibits its toxicity in higher concentration and above 50 ppm several symptoms are gradually progressive as well as anosmia.Concentration above 500 ppm causes immediate loss of consciousness and death in 30 to 60 minutes.

So,because of the toxicity of H_2S in concentration higher than I ppm and the extensive formation or accidental escape in the atmo sphere that may cause industrial and environmental problems, there exist a need for a rapid,simple and practical method for the determination of poisonous concentrations of H_2S in the environment.

This paper reports the results of an investigation on the feasibility of determining H_2S in atmosphere as well as sulfides by an indirect atomic absorption spectroscopy method.In this developed method known amound of buffered $Pb(CH_3COO)_2$ solution is added to the test sample and the excess reagent is measured by A.A.S.(Atomic Absorption Spectroscopy).This appeared to offer a simple system for handling large numbers of samples with an appreciable saving in operator's time.

Hydrogen sulfide has been determined by various methods but some of them can be applied to ambient air analysis and the most of them concern with very low concentrations of it and need large volume of air sample.The best procedure for air pollution survey and control purposes is absorption in a solution of zinc or some cadmium salt, with subsequent colorimetric estimation as methylene blue(STERN'68). This method has been studied by BUDD and BEWICK(1952) and reported by JACOBS et.al.(1957).It is based on the old method of GARDNER et

Bulletin of Environmental Contamination & Toxicology,
Vol. 15, No. 4 © 1976 by Springer-Verlag New York Inc.

al.(1927) which adopted and described by WALLACH and O'BRIEN (1951) and modified by QUITMANN(1937) and MOSKOWITZ et al.(1940).Many others various methods for H_2S determination in air by spectrophotometric,gas-cromatographic and other technics have been proposed by several authors.However despite the great nymber of publications concerning H_2S determination in atmosphere or elswhere we could't find hitherto experimental data showing the possibility of H_2S determination applying atomic absorption spectroscory. A.A.S. indirect methods have already been applied by many authors for determination of sulfates.

The proposed method is easier and more rapid to the colorimetric and gas-chromatographic methods and does not require special accesories except vacu-sampler. A.A.S. instrumentation,as routinaly used in metal toxicity studies with no modification or special attention. The proposed method can be also utilized for sulfides analysis.

Reagents and apparatus

1.-Crystalls of $Pb(CH_3COO)_2.3H_2O$ (Merck) were used to prepare a stock solution of 3000 ppm Pb.A few drops of con.acetic acid was added in order to avoid cloudness in the prepared solution. From this stock solution aliquots were taken and diluted to the desired concectration of Pb.These solutions had pH 4-4,5 and by the addidion of solid sodium acetate the pH was brought in the proximity of 5,6 before each experiment.

2.-Standard sulfide solutions were prepared freshly each time by disolving the appropriate amount of $Na_2S.9H_2O$ in bi-distilled water.

3.-Three gas washing bubblers of 300 ml each were connected in series.The first one,which was used for the generation of hydrogen sulfide was connected with a cylinder of pure N_2.The others two were utilized for trapping the H_2S in definite amounts of buffered solutions of lead acetate.

4.-Vacu-sampler MDA Scientific Inc.U.S.patent No 3,618393.

5.-A.A.S.The determination of lead reported in this peper performed with Perkin-Elmer mod 303 Atomic Absorption Spectrophotometer equiped with a Hitachi Perkin-Elmer recorder mod 150 and a three slot burner using air-acetylene flame.A Perkin-Elmer hallow lead lamp was used utilizing 283 mμ spectral line.

6.-pH meter.A WTW (WTW GMBH Germany) pH meter,model 390 was used in our experiments.

7.-Filters.Selecta filters,Schwarrzband No 589[1] Carl Schleicher & Schull Germany,diam.9 cm,were used.

Experimental

After preliminary work the following experimental procedure was followed:

Into the first bubbler were placed,each time,100 ml of a sodium sulfide solution containing the theoritical amount of 100,500,1000, 2500 and 3500 μg sulfide.Into the other two bubblers the buffered solutions of lead acetate were placed containing 1000,5000,10000, 25000 and 50000 μg lead.(100 ml,which with the washings became ~150 ml, ~2/3 in the first and ~1/3 in the second)

The system was flushed with pure N_2,at a rate of ~250 ml/min for about 3-5 minutes.While flushing 20-40 ml cold diluted(1/1) sulfuric acid was added,from a separatory funnel,over a period of 2-4 min into the first bubbler containing the standard solution of sodium sulfide.After 20-30 minutes,in which flushing was continued the heterogenous contents(*) of the last two bubblers were transferred quantitatively into a volumetric flask,so that the lead to be in the range 1-20 ppm.The precipitate was removed by filtration and in the collected clear filtrate the concentration of lead was determined by A.A.S.

Before each measurement the calibration curve verified by utilizing the standard solutions of lead acetate.

Systematic investigation of the various parameters involved was undertaken.

(*)A third trap with $Pb(CH_3COO)_2$ was used to detect any escaping from the system.No escape was noticed (absence of PbS precipit) under the experimental conditions.

Accuraty of the method

Fig.I indicates the obtained results from a series of experiments in which the lead in the filtrates was determined,by following the above experimental procedure,in comparison with the calibration curve (up to 20 ppm).

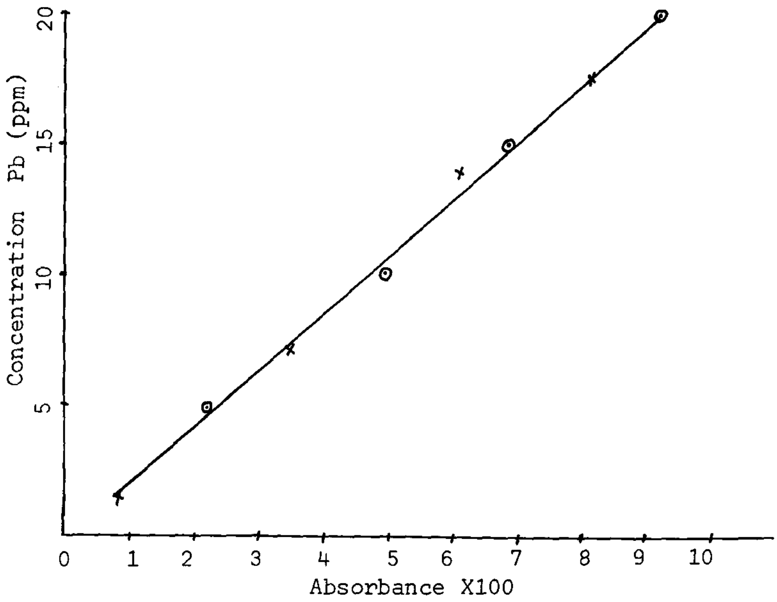

Fig.I

⊙=Standard solution of Pb(ppm)

x=Filtrates of known concentration

Flushing time

To verify the quantitative evolution of hydrogen sulfide and the minimum flushing time required for complete removal of it from the first bubbler,a series of experiments were performed with standard solutions of Na_2S and $Pb(CH_3COO)_2$.Table I below summarizes the results.

TABLE I

Flushing time min	$(S^=)$ µg/ml	LEAD µg/ml Initial	Calculated for the reaction on theoretical basis	Experim. found	Reacted (as PbS)
5	25	250	161,8	131	119
15	25	250	161,8	160	90
25	25	250	161,8	162	88
35	25	250	161,8	162	88
5	10	100	64,7	55	45
15	10	100	64,7	62	38
25	10	100	64,7	65	35
35	10	100	64,7	65	35
5	5	50	32,4	29	21
15	5	50	32,4	32	18
25	5	50	32,4	32	18
35	5	50	32,4	32	18

Effect of pH range

A series of experiments were performed by altering the pH,of the solutions of lead acetate,from 2,4 to 6,8.The extention of pH in one or in the other direction was achieved by adding small amounts of acetic acid or sodium acetate respectively.

The three sets of experiments were design so that at the end of the reaction a known excess of Pb (2,8 - 14,1 - 17,6 ppm) to remain unreacted in the solution on a theoretical basis.Fig.II illustrates the obtained results.

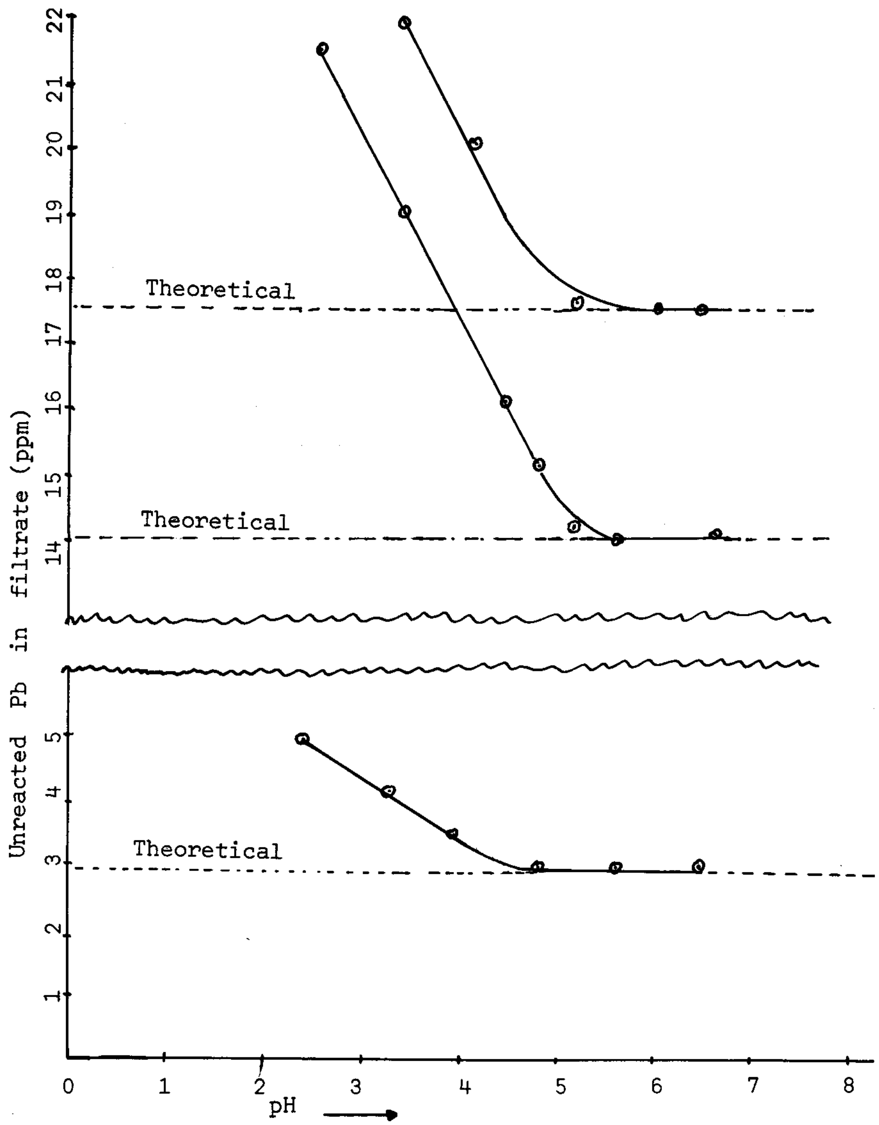

Fig.II

Solubility of PbS

It was thought that the use of buffer solutions might affect the solubility of PbS.This possibility was checked,under the same experimental conditions,and was found that the precipitate of PbS has no detectable influence upon the determination of Pb in solution.

Interferences

Generally speaking,any substance which can react with lead and forms insoluble compounds affects the accuracy of the method.Since sulfur dioxide and carbon dioxide coexist with hydrogen sulfide,in industrial and environmental atmosphere,the possible interference of these two gases was examined.

While carbon dioxide was found to have no effect at least up to concentration of 50 ppm,sulfur dioxide inderferes for the determination of H_2S.

In such a case when SO_2 or other organic sulfur compounds coexist in atmosphere together with H_2S we can remove them by adsorption on silica gel filter according to FOGO and POPOWSKI (1949).This filter although adsorbs SO_2 and organic sulfur compounds has a negligible effect on H_2S.

Applications

The determination of hydrogen sulfide by indirect A.A.S. appears to be simple,accurate and precise and may be applied:

1)For the determination of hydrogen sulfide in the environment.In the certain cases (accidental escape in industries,heavily polluted air) is needed to take samples at once for examination.For this purpose vacu-samplers (Vol.123,4 ml in temp.21°C and pres.760 mmHg) are filled with gases by simply pressing the top of them for 10-15 seconds and submitted to laboratory.The recorded data are:date,time, place,temperature and atmospheric conditions.In cases where sulfur dioxide is to be avoided a tube with silica gel is connected to inlet of the vacu-sampler and the entering gas passes through that tube.Silica gel is known to adsorbe SO_2 and allow H_2S to pass freely.

When we use this method,two vacu-samplers were filled from the same gas und r the same conditions.The one of them is used for a preliminary test and the other one for the final accurate determination.In the first vacu-sampler it was introduced a buffered solution (50 ml pH=5,6) of $Pb(CH_3COO)_2$ containing 3000 ppm.

After 30 minutes,with occusional shaking,the sampler is opened and the residual Pb was determined in filtrates by A.A.S.If the determined lead was found to be in the first sample more than 2500 ppm (H_2S less than 35 ppm) we will add in the second sampler 50 ml of the appropriate concentration lead solution pH=5,6 in order to obtain a measurable amount of lead in the range of 30% excess.

In cases where the H_2S concentration is low,a measured volume of air is passed through two traps in series containing 100 ml of a 0,5 N NaOH.The above solution is transfered quantitatively into a bubbler and from there on the procedure is the same as in the pilot experiments.

2)For determination of total sulfides in various solutions even in polluted waters.The procedure which is followed is the same as in described pilot experiments.

Discusion

The calibration curve (Fig.I) was found to be linear over the examined range 1-20 ppm Pb.It was not necessary to go beyong 20ppm because the solutions were diluted within that range,prior to determination of residual Pb.The obtained results from pilot experiments fit very well in the calibration curve.This agreement may be seen also from the flushing time experiments (Table I),where under the experimental conditions,the minimum flashing time was found around 25 minutes.

So,the accuracy and the precision of the method have been established.It seems that the limited factors is associated with A.A.S. Since the sensitivity for lead determination by A.A.S. as described above is 0,5 μg/ml for 1% absorption we concluded that it is equivalent to 0,082 μg H_2S (1 μg H_2S=6,088 μg Pb).

From Fig.II may be seen that the pH range where there is agreement between calculated and experimentally obtained results for residual lead is 4,9 - 6,6.Below pH 4,9 no complete precipitation of lead occurs with hydrogen sulfide and above 6,6 cooprecipitation of lead occurs with PbS due to formation of $Pb(OH)_2$.In all our experiments the pH of $Pb(CH_3COO)_2$ solutions was adjusted to 5,6 by the addition of small crystals of sodium acetate.This buffering process was followed because is simple and stable for one week and there was no need of making fresh buffer solutions every time.The influence of buffer CH_3COOH - CH_3COONa,under the same experimental conditions,upon the solubility of PbS was found to be negligible.The excess of $Pb(CH_3COO)_2$ should be more than 10% from the theoretical amount needed for the reaction with H_2S and in our model experiments the excess was kept around 30%.An additional advantage of the method is that by using excess Pb^{+2} the solubility of the formed PbS is depressed by means of common ion effect.

All interferences due to SO_2 or organic sulfur compounds may be avoided using a silica gel filter.

We checked our technic ur to 200 ppm of hydrogen sulfide using a buffered solution of lead 3000 ppm and we had good agreement with theoretical and found results.

Acknowledgements

We wish to express our appreciation to Dr.Ch.Gatzonis for helpful discussions and assistance to write the manuscripts.

References

BUDD M.S. and BEWICH H.A.,Anal.Chem. 24,1536,(1952).
FOGO J. and POPOWSKY M.,Anal.Chem.21,734,(1949).
GARDNER E.D.,HOWELL S.P. and JONES G.W.,U.S.Bur.Mines Bull.287(1927)
JACOBS M.B.,BRAVERMAN M.M. and HOCHHEISER S.,Anal.Chem.29,1349(1957)
MOSKOWITZ S.,SIEGEL J. and BURKE W.J.,M.Y.State Ind.Byll.19,33,
(1940).
QUITMANN E.Z.,Anal.Chem.109,241(1937).
STERN A.,Air Pollution,vol.II,p.78,Academic Press N.Y. 1968
WALLACH A. and O'BRIEN E.P.,Proc.Montana Acad.Sci.10,39,(1951).