Analyte volatization procedure for determination of low concentrations of Sulfide Content in Lead

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Abstract: A method for determination of sulfide based on chemical evaporation of sulphide to hydrogen sulphide and following by potentiometric measuremen has been developed. Simple equipments, sufficient sensitivity and low running cost are the important advantages of this method.

Keywords: Chemical evaporation, hydrogen sulfide, potentiometric measurement, sulfide

1. Introduction

In lead, sulfure mainly exists in a chemical form as lead sulphide (PbS) [1] and deteriorates metallurgical properties of lead. In high quality lead product, the sulphur content is reduced to very low levels, the less than $20\mu gg^{-1}$ in a soft lead, for example. Therefor there is a great need of development of a rapid and sensitive method for the determination of sulfur for controlling the lead making process and and product quality. Production of valve regulated lead acid (VRLA) Batteries requires to high purity lead or soft lead [2]. During the last years, many studies have been reported of sulfure content in liquid or silid samples. Many of them imply the reduction of the sample with appropriate reagents in order to convert its total sulfure in to gaseous hydrogen sulfide, which is absorbed in a basic solution and analysed by standard procedure. In spite of the huge progress chemical analytical techniques, the sulfur group determination in a lot of solid matrics still suffers from many deficiencies [3-6].

Potentiometry with ion- selective electrodes is, at least in principle, not limited by such scaling laws as the observed potential is a direct function of the sample ion activity, independent of the sample volume [7-9].The aim of this study was to elaborate a simple and rapid method of sulfur determination in solid matrics, a method that would be sensitive enough to distinguish sulfur content in some industrial products. Optimization of experimental parameters and analytical figures of merit under the optimized conditions are given. Finally the application of the present technique in soft lead and water samples is described below.

2. Experimental

2.1 Apparatus

ISE measurements were carried out using an Orion silver/sulphide electrode (model 94-16) and an Metrohm Ag/AgCl refrence electrode with 3.5 M KCl in the outer compartment. A digital Potentiometer (Metrohm model) was used for all Potentiometric measurement . The
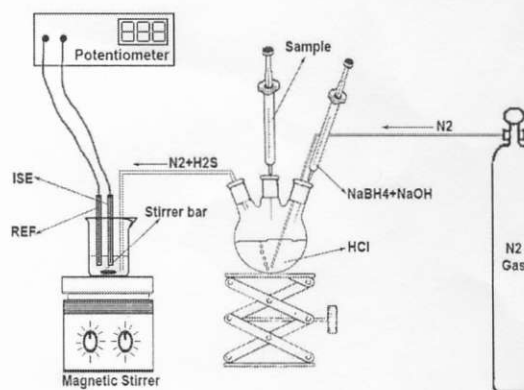

Fig. 1: the apparatus to analyse sulphur content in solid samples.

TABLE I: Optimized variables for proposed procedure.

Parameter	Evaluated range	Optimum condition
Volume of H_2S producing solution	10-25	10 ml
HCl Conc.	0.6-1.4	0.8 M
$NaBH_4$ %	1-5	2
%NaOH in $NaBH_4$	2-10	6
Temp. in H_2S producing solution	0-40	8?C
Carrier gas flow rate	5-25	10 ml/min
Temp. in H_2S collecting solution	0-60	25?C
NaOH Conc. in H_2S collecting solution	0.032-0.7	0.612 M
Volume of collecting solution	15-45	25 ml
Time of analysis	0-30	10 min

apparatus shown in Fig. 1 was used.

3.2 Reagents and Solutions

Analytical reagent grade were used without further purification. De-aerated water and N_2 gas with high purity were used in all experiments.

A sulfide solution was prepared from large crystals of sodium sulfide ($Na_2S.9H2O$) using oxygen free water. The crystals were washed rapidly with water in order to remove any trace amount of impurities from their surface and then dried by absorption of the water with filter paper. An approximately 0.05 M sulfide solution was prepared by dissolving approx. 2.5 g of the crystals in 200 ml of oxygen-free water and then standardized iodimetric back-titration.

The sulfide anti-oxidation Buffer (SAOB) solution was prepared by mixing 200 ml NaOH (10 M), 3.5 g ascorbic acid(Merck, >99.5%), 6.7 g Na_2(EDTA) (Merck) and deionised-deaired water to get 1 L solution. This solution was stored in a tightly caped brown glass bottle and discarded when the solution becamed discoloured.

2.3 Analytical Procedure

This procedure generally consist of two phase. The first, is related to extraction of sulfide as hydrogen sulfide and the second, measurement of it. At the first place, HCl introduced in glass device. After deaerating the system by passing N_2 gas, by using two syringes, the sulfide samle and $NaBH_4$ are added to glass device. The stabilization time by using optimum conditions takes up 10 min. Before series of measurements of sulfide, the silver-sulfide electrode Was calibrated with standard solution of sodium sulfide in the buffer solution.

3. Results and Discussion

3.1 Optimization of parameters

Optimization of experimental parameters was investigated based on the differences of sulfide selective electrode in sample measurement and final potential of ISE in the blank experiment. Through out of this section, the aim has been maximum change in sample rather than blank. All the variables studied and their optimum values foud are listed in Table 1.

3.2 Analyte Evaporation

The lead sample dissolved in nitric acid or standard solution was injected to system to form hydrogen sulfide.

Present of sodium borohydride reduced analysis time. In present of sodium borohydride, the signal arise to maximum quickly.

3.3 comparasion of direct and indirect measurement of sulfide

The direct measurement was performed by addition of sulfide standard solution to vessel of containing electrodes, and indirect measurement was performed by injecting 5 ml standard solution to vaporation cell.
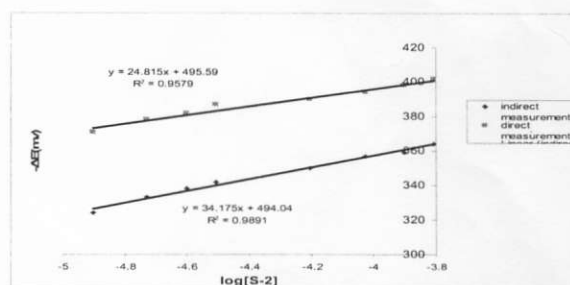

Fig 2.: comparasion of direct and indirect measurement of sulfide.

TABLE II: Feathres of the method.

Analyte	Linear range (ppm)	Equation [a]	R^2	Sensitivity (ppm^{-1})	LOD[b] (ppm)	RSD[c](%)
Sulfide	0.4-5	$E = 34.2\,C + 494$	0.9891	34.0175	0.4	0.67

[a]E = potential in mv; C= logarithm of sulfide concentration in molarity, [b] experimental LOD and [c] At $1\mu gml^{-1}$ sulfide (n= 5)

The obtained results are shown in Fig. 2. According the results, In direct measurement, the slope of calibration curve is nernstian (26±3), while in indirect method its higher. Therefor in the later, we have more sensitivity, lower volume of sample solution and removing the interferences.

3.4 Analytical figures of merit and Accuracy

The performance of the proposed approache for the determination of sulfure was evaluated for the linear dynamic range, limit of detection and precision. They are listed in Table 2.

The prodedure was employed to determine sulfide in lead and real water samples. The results are summerized in Table 3.

For determination of sulphur in soft lead, 0.5 g of sample was dissolved in 4M nitric acid . The amount of sulphur 9±0.5 was approximated.

TABLE III: Experimental recovery on sulfide determination in water sample spiked with 1.0, 2.0 and 3.0 μgml^{-1} of sulfide

Sample	Sulfide ppm		Recovery (%)
	Added	Found	
Real water sample	1	0.92	92
Real water sample	2	2.05	102.5
Real water sample	3	2.83	94.3
			Avg. =96.3

4. Coclusion

The developed analytical system provided a rapid determination of sulphur in lead. It can determine low amount of sulphur with a relative standard deviation of 0.67 % and a measurement time of 15 min. Furthermore, it can be applied to other matrices as well as lead. Consequently, the analytical system is essentially suitable for process control and/or quality control of lead making processes at production sites.

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