

Determination of Lead in Aqueous System by Flow Injection Technique Coupled with Spectrophotometer

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(Received 13th August, 1994, revised 30th September, 1995)

Summary: A spectrophotometric flow injection procedure for the determination of lead is described. The procedure is based on measurement of absorbance from the colour produced by the reaction of lead with sodium sulfide in the presence of ammonia. Results are presented for lead at a sample throughput of 60 h⁻¹ and repeatability is 1.5% at 1000 mg/dl. The method is well demonstrated by analyzing lead in lead-ores which were pre-determined by using atomic absorption spectroscopy.

Introduction

There has been a growing interest to control pollution which is a serious threat to our environment. Amongst a variety of factors resulting from human activities, those involving heavy metals are most dangerous, their toxicity is beyond doubt. The distribution of lead in the atmosphere spreaded mainly due to vehicles utilizing leaded petroleum attract public concern [1]. Lead contamination also arise as a result of the use of lead pipes, tanks and industrial effluents [2]. The European community standards are stipulated quantitatively in terms of maximum admissible concentrations (MACs) the guide line for lead concentration in water [3].

There are several methods reported for the determination of lead, principally by spectrophotometry [4], amperometry [5], atomic absorption spectroscopy [6,7] and enzymatic analysis [8]. Spectrophotometric methods are still the most commonly used methods of analysis. Most

of spectrophotometric methods developed are based on solvent extraction followed by chelation with diethylenetriamine which is subsequently measured by a spectrophotometer [9]. The extraction in organic phase requires phase separator which make use of the difference in density of two phases and employes phase-separation [10].

This study presents flow injection procedure for the determination of lead in aqueous medium. The procedure is simple, rapid and does not involve phase separation. The method is applied to the determination of lead in lead-ores and the results were compared with atomic absorption spectroscopy.

Results and Discussion

The reaction conditions with respect to flow rate and reaction coil length were optimized for lead determination. The results shown in Table-1,

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indicate the faster rate of lead reaction and therefore gives a faster throughput of samples. Increase in the flow rate increased the absorbance due to rapid sample dispersion in the reaction coil. Increasing the reaction coil length decreased the absorbance due to faster kinetics of the lead reaction and dispersion of sample at longer residence time. However for higher sample throughput and better reproducibility a coil length of 30 cm is used for subsequent experiments. Table-2 shows the effect of various reagents on the rate of formation of lead sulfide. The effect of lead sulfide was studied over the range of 0.01 - 1000 mg/dl while keeping all the variable constant. The absorbance increased from 0.01 - 100 mg/dl. Above 100 mg/dl no appreciable increase in absorbance was observed due to the saturation of other reagents with respect to sodium sulphide.

The effect of ammonium acetate and sodium citrate over the range ($1 \times 10^{-7}M$ - $1 \times 10^{-2}M$) have shown very little effect on the absorbance and the involvement of these reagents in the media is to avoid precipitation and interferences. The effect of ammonia solution was also checked to its basicity for the formation of lead sulphide. A concentration level of $1 \times 10^{-4}M$ was found to be suitable and used for further studies.

Calibration data for lead

The calibration data for aqueous lead standards over the range of 0.1 - 1000 mg/dl are presented in Table-3. The overall relative standards deviation was less than 1.5%. The response in absorbance is linear over the range of 1.0 - 10 mg/dl and no blank signal was obtained which show that the method developed is attractive for lead analysis in environmental samples. To demonstrate the performance of the established method lead sample was selected which was pre-determined for lead by using atomic absorption spectrophotometer [11,12]. The lead concentration found in the sample was 2.5 mg/dl. The reason for selecting the above sample was that its concentration determined by the atomic absorption falls within the linear range of the method developed. The concentration of unknown lead calculated from the calibration graph was found to be 2.5 mg/dl. The values obtained by both the methods are in good agreement with each other.

Table-1: Effect of reaction coil length and flow rate.

Flow rate ml/min	Absorbance*	Reaction coil length (cm)	Absorbance*
1.5	0.042	15	0.045
2.0	0.043	30	0.038
2.5	0.044	60	0.038
3.0	0.046	100	0.029
3.5	0.051	150	0.028
4.0	0.054	200	0.025

*Mean of three readings.

Table-2: Effect of reagents on absorbance

Sodium sulfide (M)	1×10^{-7}	1×10^{-6}	1×10^{-5}	1×10^{-4}	1×10^{-3}	1×10^{-2}
*Abs	0.001	0.002	0.004	0.006	0.038	0.034
Ammonia (M)						
*Abs	0.026	0.028	0.031	0.032	0.020	0.020
Ammonium Acetate (M)						
*Abs	0.036	0.040	0.041	0.042	0.038	0.036
Sodium citrate (M)						
*Abs	—	0.023	0.033	0.034	0.032	0.026

*Mean of three injections.

Table-3: Calibration data for lead determination

Lead concentration mg/dl	Absorbance*	R.S.D.(%)(n = 3)
Blank	0.000	—
0.1	0.002	2.0
0.5	0.005	1.9
1.0	0.008	1.0
5.0	0.020	0.6
10.0	0.041	0.6
50.0	0.286	1.0
100.0	0.572	1.2
1000.0	1.782	1.5
Unknown	0.014	1.2

*Mean of three injection

Table-4: Effect of diverse ions on lead determination

Diverse ions	Concentration mg/dl	Absorbance*
Lead (11)	10.0	0.041
Iron(111)	—	0.041
Magnesium(11)	100.0	0.001
Cobalt(11)	10.0	0.022
Copper(11)	—	0.006
Chromium(11)	—	0.002
Nickel(11)	—	0.001
Zinc(11)	—	0.001
Cadium(11)	—	0.027

*Mean of three injections.

Interferences

Table-4 shows the effect of various cations and their concentration on the absorbance compared with lead (10 mg/dl). The only significant interferences are Cd(II), Co(II) and Fe(III), which had positive effect on absorbance.

These could be removed by suitable masking reagents.

Experimental

All reagents employed were of analytical reagent grade (Merck, BDH) and distilled/deionized water was used throughout the experiments. Sodium sulphide solution (0.01 M) was prepared fresh whenever required by dissolving 0.24 g of AnalaR sodium sulphide in 100 ml of water. The crystals were initially rinsed with water. Lead nitrate solution (1000 mg/dl) was prepared by dissolving 0.33 g of lead nitrate in 100 ml of water. Standards for the required range of concentration were prepared by serial dilution of this stock solution. Ammonium acetate (0.1 M) was prepared by dissolving 0.8 g of the compound in 100 ml of water. Acetate solution (0.01 M) was prepared by dissolving 0.3 g of the compound in 100 ml of water. Ammonia solution (1.0 M) was prepared by diluting 5.9 ml of ammonia (33%) to 100 ml with water. Lead ores were collected by the Geological Survey of Pakistan from Kirana Hills, District Sargodha, Punjab Pakistan. Samples were dissolved according to the procedure mentioned before [13].

Instrumentation and procedure

Initial measurements of lead were carried out manually by using spectrophotometer (Jenway, 6100, U.K.) fitted with 1.0 cm cuvette. All flow injection measurements were made by using Spectrophotometer (Hitachi, 1100, Japan). Fig. 1,

shows a flow injection manifold for the determination of lead. Leads standards (30 μ l) were injected via PTFE rotary valve (Rheodyne 5020) into a stream of ammonia containing ammonium acetate (21×10^{-4} M) and sodium citrate (1×10^{-5} M) was merge 15 cm downstream with sodium sulfide (1×10^{-3} M) containing ammonia (1×10^{-4} M) at a PTFE T-piece. The standards and reagents were allowed to mix in a 30 cm mixing coil. The absorbance due to the formation of coloured compound by the reaction of lead and sulphide in basic media was monitored at 420 nm using a spectrophotometer with a flow through cell (30 μ l). The manifold tubing were teflon (0.8 mm i.d.). The reagent streams were pumped at the same flow rate (1.2 ml min⁻¹) by a peristaltic pump (Autoclade Model VL). The signal of the detector output were recorded using a strip chart recorder (Kipp and Zonen BD 40). The procedure for ores analysis were the same as used for the lead standards. Atomic absorption spectrophotometer Model Spectra AA-20 (Varian, Australia) is used to determine lead in ores according to the procedure [12].

Conclusion

The combination of flow injection with spectrophotometer provides a simple, rapid and inexpensive mean of determining metal ions in trace levels. The aqueous system is attractive as compared with extraction of metal in organic phase and then its determination. Methods for eliminating interfering elements will allow a highly selective determination of lead in real samples.

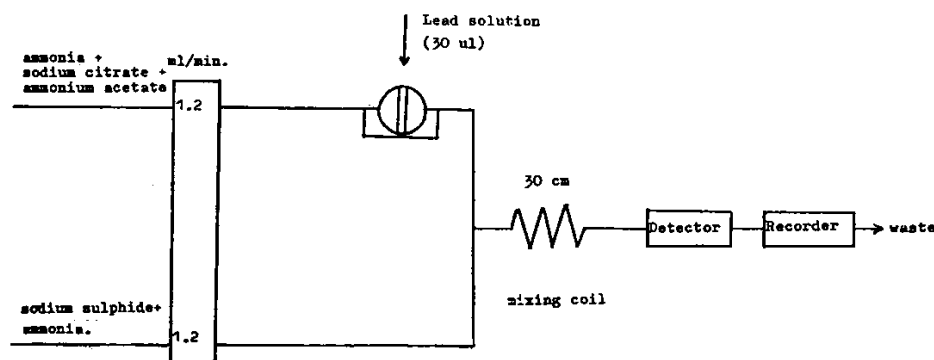


Fig.1: Flow injection manifold for the determination of lead.