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Clean analytical methodology for the determination of lead with Arsenazo III by cyclic flow-injection analysis

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Abstract

A clean analytical methodology, where the sample determined and the reagent used are both toxic, has been proposed. A cation exchange mini-column was incorporated after the flow-through cell for on-line regeneration of the main reagent and the accumulation of heavy metal ions. The method involves the spectrophotometric determination of lead with Arsenazo III, the accumulation of lead onto the cationic exchanger, and subsequent regeneration of the chromogenic reagent, which makes the system reversible and the reagents reusable. The developed method provides a satisfactory way to cut down on the toxic reagent consumption and the produced volume of waste, an important step towards the zero emissions research initiative concept. The excellent repeatability and reproducibility, and the simplicity of this method are well suited for continuous measurements. The method was successively applied to the assay of lead in high-octane gasoline.

Keywords: Cyclic FIA; Clean analytical method; Lead; Arsenazo III

1. Introduction

Flow-injection analysis (FIA) is now widely used in analytical measurements. Compared to the batch-wise method, low reagent consumption as well as small sample size is one of the advantages of FIA [1]. But all methods proposed do not mention anything about the final wastes, which could be very toxic and polluting [2]. In conventional FIA, carrier and reagent solutions are continuously fed to flow system, therefore, the hazardous sample injected is diluted with both the carrier and the reagent solution. Because the sample solution is not always injected in the system and sample size is too small, the sample is diluted unnecessary and the volume of wastes increases in large excess. Highly diluted wastes need more extensive effort and cost. It is essential to control the wastes from this kind of measurements in order to prevent laboratories engaged in this field of analysis from being additional sources of contamination. Hence, detoxification of the final products or minimization of wastes must be taken into consideration as an additional step in analyses of hazardous products that involve the use of toxic reagent.

Cyclic FIA, which affords the recirculation of the same reagent solution, leads to an appreciable answer to a clean analytical method [3–5]. To avoid the undesirable pollution, we have studied cyclic FIA in order to reuse the reagents employed and to minimizing the waste produced. Some approaches based on the reversible reactions have been proposed [6–9].

For a clean analytical method, a cyclic FIA of lead with Arsenazo III has been proposed as a model system. Arsenazo III is a well known and widely used spectrophotometric reagent for several metal ions. It reacts with lead to form a sensitive complex ($\varepsilon = 2.8 \times 10^4\,\mathrm{l\,mol^{-1}\,cm^{-1}}$ at 600 nm) in a weakly acidic solution [10,11]. Unfortunately, Arsenazo III has two arsenic acid groups in a molecule, so is highly polluting. On the other hand, lead, which produces several diseases is one of the most important and widely distributed pollutants in the environment [12]. It must be recognized that the conventional FIA is inappropriate from the environmental point of view, because for the determination of lead, the method involves the use of Arsenazo III which is continuously fed

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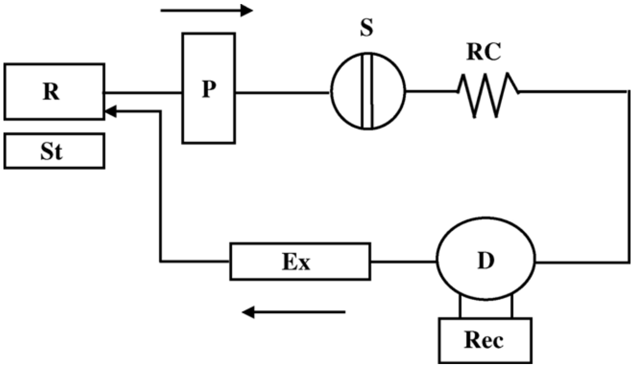

Fig. 1. Schematic diagram of a cyclic flow-injection system for the determination of lead. R: reservoir; P: pump; S: sample injector; RC: reaction coil; D: detector; Rec: recorder; Ex: ion-exchange column; St: stirrer.

to the flow system and thus, provides a potential source of environmental contamination due to the presence of arsenic and lead in the waste. It is necessary to develop strategies for minimizing the waste containing.

In this paper, a cyclic FIA is adopted for the determination of lead with Arsenazo III, thereby providing a closed-flow system with waste-less procedure, simple handing and high sample throughput. This system is skillfully applied to the determination of lead in high-octane gasoline, providing a non-polluting method of analysis.

2. Experimental

2.1. Chemicals

Analytical reagent grade chemicals and ultra pure water from a Milli-Q water system were used throughout. Arsenazo III was purchased from Dojindo Laboratories (Kumamoto, Japan) and used without further purification. A lead standard solution (1000 mg l^{-1}) was purchased from Wako Pure Chemicals (Osaka, Japan). Commercially available cation exchange resins, Amberlite IR122, IR124Na and 200 (strongly acidic type, 16–50 mesh, 2.1, 2.2 and 1.7 meq ml^{-1}, respectively), and IRC76 and IRC748 (weakly acidic or chelate type, 16–50 mesh, 4.0 and 1.25 meq ml^{-1}, respectively) were used in the Na^+ form.

2.2. Apparatus

A schematic diagram of the flow system used in this work is shown in Fig. 1. The FIA apparatus, consisted of a double-plunger pump (DMX-2300, Sanuki, Japan), a six-way rotary valve (9725, Rheodyne, 20 μl loop), a visible spectrophotometer (S-3250, Soma, Japan) equipped with a flow-through cell (1 cm light path, 18 μl inner volume) and a multi-range recorder (U-228, Nippon Denshi Kagaku, Japan). A column was prepared by packing an appropriate amount (ca. 0.5 g) of a cation exchanger into a 7 cm × 4 mm i.d. glass tube for the regeneration of the free Arsenazo III, and was placed after the flow-through cell. Flow lines were made of PTFE tubings (0.5 mm i.d.) and connectors.

2.3. Procedure

A typical circulating reagent solution was made up of 50 ml containing 1.0×10^{-4} M Arsenazo III in 0.1 M acetate buffer (pH 4.7). This solution in the reservoir was constantly stirred with the help of a magnetic stirrer, and pumped to the single-line FIA system at a flow rate of 1.5 ml min^{-1}. In the determinations, 20 μl of standard/sample solutions was injected into the reagent stream, the formed complex was monitored spectrophotometrically at 655 nm and the response was fed to a strip chart recorder. After passing through the flow-through cell, the stream was carried into a mini-column (7 cm long, 4 mm i.d.) to accumulate lead onto the cation exchanger and to regenerate the free Arsenazo III, and then carried back to the reservoir.

2.4. Sample preparation

For the determination of lead, the appropriate weight of the standard gasoline was leached with a 1:1 mixture of 1 M iodine monochloride solution [13]. The mixture was heated to 60 °C in a water-bath for 2 min. Then the aqueous phase with extracted dialkyl-lead compounds is evaporated to dryness with addition of concentrated nitric acid. The residue is dissolved in water, and 20 μl of this solution was directly injected into the circulating reagent solution.

3. Results and discussion

Because Arsenazo III has two sulfonic acid groups in a molecule and forms a water-soluble anionic complex with lead having a metal–ligand ratio of 1:1 [7,8], preliminary batch-wise experiments revealed that Arsenazo III and its lead complex were not adsorbed onto the cation exchangers. The equilibrium constant of the cation exchanger-Pb^{2+} is larger than that of Arsenazo III–Pb^{2+} complex, the following ligand-exchange reaction between the lead complex and a cation exchanger occurred:

$$\text{Arsenazo III} - Pb^{2+} + Ex \rightarrow \text{Arsenazo III} + Ex - Pb^{2+}$$

where Ex represents a cation exchanger. As the results, lead was strongly held and accumulated onto the cation-exchanger, and the free Arsenazo III was regenerated and could be reused repeatedly. This made it possible to adopt the cyclic FIA system and to determine lead repetitively.

3.1. Optimization of chemical and FIA variables

The selection of the reservoir volume should be dictated mainly by the number of samples to be determined and the approximate content of the analyte. Taking into account an effective reuse of the toxic reagent and minimizing the waste,

Table 1
Optimum conditions found for the cyclic FIA system

Variables	Optimal value	Range studied
Reservoir volume (ml)	50	–
Arsenazo III (mmol l^{-1})	0.1	0.05–0.5
Acetate buffer (mol l^{-1})	0.1	0.01–0.5
pH	4.7	2.0–7.0
Injection volume (μ l)	20	5–100
Reaction coil length (cm)	100	100–200
Flow rate (ml min^{-1})	1.5	1.0–2.25
Wavelength (nm)	655	400–700
Ion-exchanger weight (g)	0.5	0.1–0.5
Column (0.4 cm i.d.) length (cm)	7	6–15

the reservoir volume (volume of the circulating reagent solution) was chosen to be only 50 ml in this work. Therefore, this volume is equal to the final waste.

Other FIA variables were optimized by using the universal method, on the basis of maximum sensitivity, adequate sampling rate and linear calibration range. The FIA variables optimized, the range studied and the optimal values are shown in Table 1.

3.2. Mini-column for regeneration of Arsenazo III

The on-line column packed with a cation exchanger was attached behind the flow-through cell (Fig. 1), and commercially available strongly and weekly acidic cation exchangers, and chelate resins were tested for the regeneration of free Arsenazo III from its lead complex. A lead standard solution (5 ppm) was continuously injected a hundred times, and the changes of flow signals (peak height, peak shape and baseline drift) were investigated. The results are shown in Fig. 2. Without a column, the baseline increased vigorously owing to the accumulation of the Arsenazo III–Pb^{2+} complex (Fig. 2(a)). And the signal strength after a hundred injections is smaller than that of the first injection because of the consumption of the free Arsenazo III.

Owing to the slow rate of ion-exchange reaction, the slight increases of baseline were observed when strongly cationic exchangers, Amberlite IR122, IR124Na and 200 were used (Fig. 2(b–d)). The best results were obtained when weakly cationic exchanger, IRC 76 and IRC748, were used. The flow signals were quite stable and resulted in good repeatability and a rapid baseline restoration (Fig. 2(e and f)). Particular attention should be given to the adsorption of the metal complexes and the chromogenic reagent, itself, on an ion-exchanger. Yoshimura and co-workers [14,15] have reported that some transition–metal complexes were adsorbed on an ion-exchange resin, and that the cell packed resin was measured directly by spectrophotometry. As they suggested, the species that were adsorbed on the ion exchanger were positively charged and converted into a complex of higher ligand number. Because Arsenazo III has two sulfonic acid groups in a molecule and forms water-soluble anionic complexes with several metal ions, having a metal–ligand ratio of 1:1 [10,11], the adsorption of Arsenazo III, itself, and its lead complex on a cation exchanger may be neglected. It is clear that the equilibrium constant of the cation exchanger-Pb^{2+} is larger than that of Arsenazo III–Pb^{2+} complex, so that the ligand-exchange reaction between Arsenazo III–Pb^{2+} complex and a cationic exchanger took place immediately, and lead was strongly held onto the cationic exchanger resulting in the release of the free Arsenazo III.

The effects of the resin weight on the regeneration of Arsenazo III were investigated using strongly cationic (Amberlite IR124Na, Fig. 3(A)) and weakly cationic exchangers (IRC748, Fig. 3(B)). When a strongly cationic exchanger was used, the baseline restoration was improved with increasing the resin weight (Fig. 3(b–d)). This is due to the slow rate of ion-exchange reaction. On the other hand, a weakly cationic

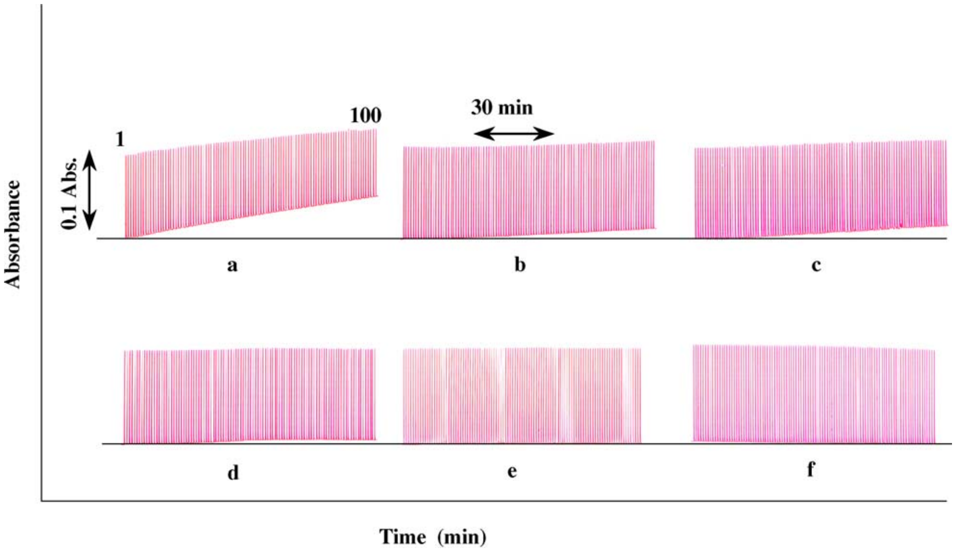

Fig. 2. Comparison of ion-exchangers on the repetitive flow signals. Resin (Amberlite): (a) nothing; (b) IR122; (c) IR124Na; (d) 200; (e) IRC76; (f) IRC748. Resin weight: 0.5 g. Pb^{2+} concentration: 5.0 mg l^{-1}.

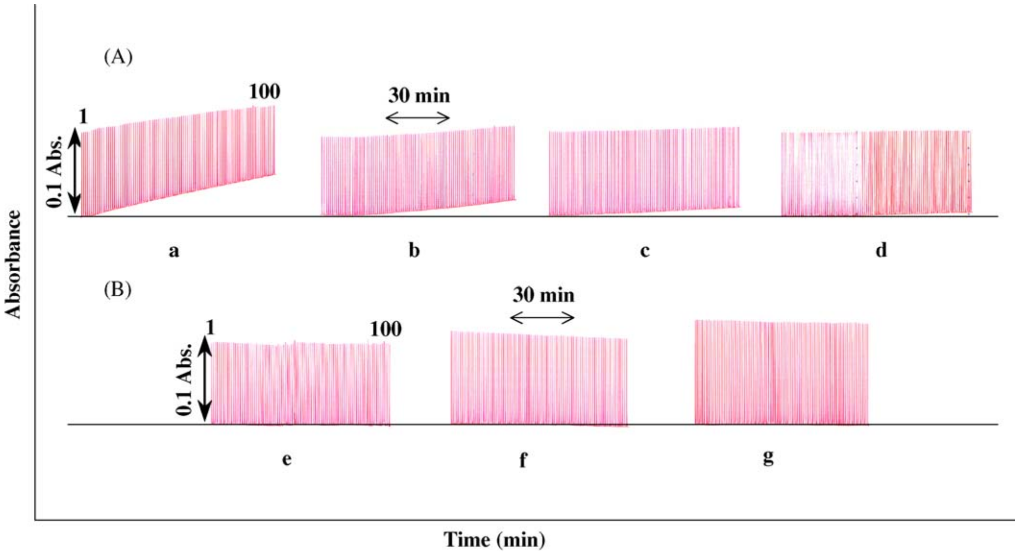

Fig. 3. Effect of resin weight on the flow signals. Resin weight (g): (A) Amberlite IR124Na; (a) without resin; (b) 0.1; (c) 0.5; (d) 1.0. (B) Amberlite IRC748; (e) 0.1; (f) 0.3; (g) 0.5. Pb^{2+} concentration: 5.0 mg l^{-1}.

exchanger with the complex formation reaction showed fast reaction rate and excellent regeneration ability even with 0.1 g packing. The peak height (sensitivity) increased with increasing of resin weight, because the impurities containing in Arsenazo III were also accumulated onto the cation exchanger and thus the concentration of the free Arsenazo III increased. The weakly acidic exchanger (IRC748) was used for further experiments.

3.3. Removal and accumulation of heavy metals

Arsenazo III is a sensitive reagent for several metal ions, but is not selective [10]. To investigate the effectiveness of the column for the removal and accumulation of the interfering ions, the lead standard solutions containing several heavy metal ions were injected into the circulating reagent solution, and the three sets of these examinations were carried out repeatedly (Fig. 4). Aluminium, copper and nickel were interfered seriously for the determination of lead; however, no significant damage was observed in either the stability of the baseline or the subsequent determinations. Lead and heavy metal ions were held and accumulated onto the cation exchanger, so that the system keeps stable and clean. Therefore, the mini-column plays as a regenerator of the main reagent, an accumulator of heavy metal ions, and a backpressure column.

3.4. Repetitive determination and robustness

The calibration graph for lead was linear in the concentration range from 0.2 to 25 mg ml^{-1} with a detection limit of 0.04 mg l^{-1}. The precise of the proposed method was tested thoroughly by a hundred repeated injections of standard solutions (1, 2, 3, 4 and 5 mg l^{-1}). The relative standard deviations obtained were 1.85, 0.44, 0.83, 0.99 and 0.88, respectively. The peak heights after a hundred injections against that of the first injection were in the range of 95.6–99.3%.

To evaluate the repeatability and stability of the response, the standard lead solutions (0–5 mg l^{-1}) were injected in triplicate for making the calibration graph, a 3 mg l^{-1} standard lead solution was injected 100 times in sequence for the regeneration and the repetitive determination test, and the calibration followed again. The intervals of each injection were one minute. The two equations for calibration graphs were coincided well [$y = 0.0128x + 0.0343$ (first injection) and $y = 0.0131x + 0.0308$ (after 100 injections), with a regression coefficient of 0.9993 and 0.9994, respectively]. No drift of the baseline should be enable to permit considerably increase the number of the sample amenable to determination with a fixed amount of the reagent. Another experiment, 300 repetitive determinations of 5 mg l^{-1} lead standard solution (5 h continuous running) showed the slight decreasing baseline. This is due to the decrease of Arsenazo III concentration in the circulating reagent solution, because the reagent solution is replaced by the same amount of sample solution on every injection. By considering the ion exchange capacity and charging, more than 1000 determinations can be carried out, if 500 ml of reservoir volume is used instead of 50 ml.

The system was run continuously for 7 days using the same circulating reagent solution (50 ml), and at daily intervals the lead standard solutions (0–5 mg l^{-1}) were injected and calibration graphs were made to compare each other. As can be seen in Fig. 5, no disturbances of the baseline were observed and the reproducible calibration graphs were obtained. It is not necessary to prepare the reagent solution and to refill the reservoir during the experiment. Therefore, this method is

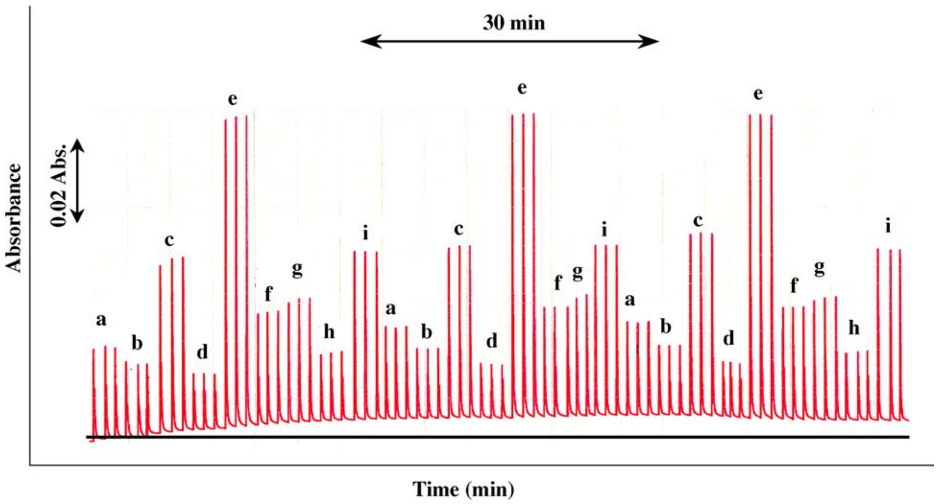

Fig. 4. Flow signals obtained by injections of lead and heavy metals. Concentration (mg l^{-1}): (a) 1.0 Pb^{2+}; (b) 1.0 Pb^{2+} + 10.0 Mn^{2+}; (c) 1.0 Pb^{2+} + 10.0 Cu^{2+}; (d) 1.0 Pb^{2+} + 10.0 Cr^{6+}; (e) 1.0 Pb^{2+} + 1.0 Al^{3+}; (f) 1.0 Pb^{2+} + 1.0 Fe^{3+}; (g) 1.0 Pb^{2+} + 1.0 Cd^{2+}; (h) 1.0 Pb^{2+} + 10.0 Hg^{2+}; (i) 1.0 Pb^{2+} + 10.0 Ni^{2+}.

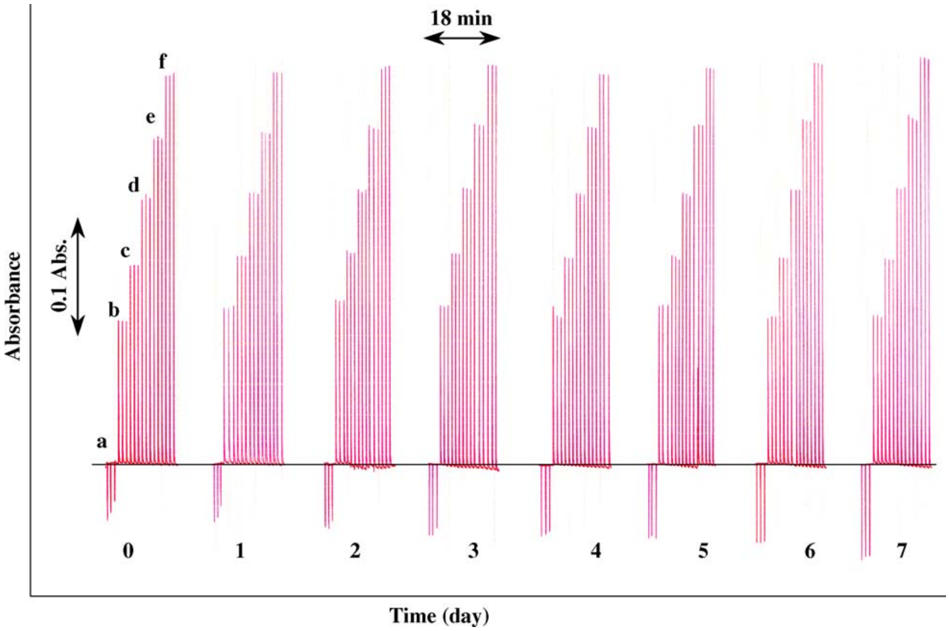

Fig. 5. Flow signals for the calibration graphs measured at 1 day intervals. Pb^{2+} concentration (mg l^{-1}): (a) 0; (b) 1.0; (c) 2.0; (d) 3.0; (e) 4.0; (f) 5.0.

suitable whenever the determining or monitoring of lead is desired. Another important feature of the proposed method is that there is no potential adsorption of the Arsenazo III and its lead complex on the cationic exchangers and wall of the PTFE tubing.

3.5. Analysis of real samples

As mentioned above, Arsenazo III is non-selective reagent so that its application to real samples is limited. It is well known that organic lead compounds are

Table 2
Determination of lead in gasoline standards

Standard[a]	Sample taken (g, ml)	Certified value	This method (mg l^{-1})	R.S.D. (%, $n = 5$)	Recovery (%)
AR-3113	1.0536 g	40 μg g^{-1}	40.5	0.27	101.3
	2.0135 g		38.3	0.18	95.8
AR-2066	0.5 ml	88 mg l^{-1}	72.5	0.38	82.4
	1.0 ml		85.1	0.09	96.7

[a] Standard samples were obtained from Alpha Resources, Inc.

added to gasoline as an anti-knock agent. The proposed cyclic FIA was successfully applied to the analysis of two standards of lead in high octane gasoline (AR-3113 and 2066). Five replicate injections for each sample were made in all instances. The results obtained are summarized in Table 2. The results obtained are in good agreement with those of the certified values except for AR-2066.

4. Conclusions

The procedure developed allows on-line recycling of the reagent solution, permitting a drastic reduction of the reagents consumption and the waste, and thus providing an environmentally friendly method. The advantages of this method also include the removal of toxic lead from the reagent carrier solution and on-line accumulation of lead and heavy metals onto a cation exchange column.

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