

## On-line Solvent Extraction of Lead and Zinc in Air Particulates

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Colored dithizone complexes, dithizonates, usually red or purple, are formed when diphenylthiocarbazonate in carbon tetrachloride reacts with metals. By controlling the pH, use of buffer and complexing agents, the reaction is made specific to a certain metal. Lead and zinc can be extracted by dithizone at pH 8.5 and 4.0–5.0 respectively. This approach was used for the development of a flow injection technique for the determination of both metals.

Optimized conditions were achieved at 150  $\mu\text{L}$  sample volume, 10 mg/L dithizone solution and 200 cm (Zn)/300 cm (Pb) reaction coils. Lead and zinc particulate samples ranged from 0.383–0.550  $\mu\text{g/L}$  and  $1.15 \times 10^{-6}$ – $5.53 \times 10^{-6}$   $\mu\text{g/L}$  respectively.

**Keywords:** flow injection analysis; on-line solvent extraction; zinc; lead; diphenylthiocarbazonate; dithizonates

### INTRODUCTION

Metal analyses have been a long time favorite for chemists [1–3]. Lead and zinc are among the many toxic metals contaminating natural bodies of water [4]. Trace amounts of these metals are now present even in air. By conventional spectrophotometric methods, these two metals can be determined in three basic steps: (1) reaction of the metal with a chelating agent such as diphenylthiocarbazonate (dithizone), (2) solvent extraction of the purple dithizonate complex, and (3) spectrophotometric detection of the colored complex. The reaction is shown in Fig. 1.

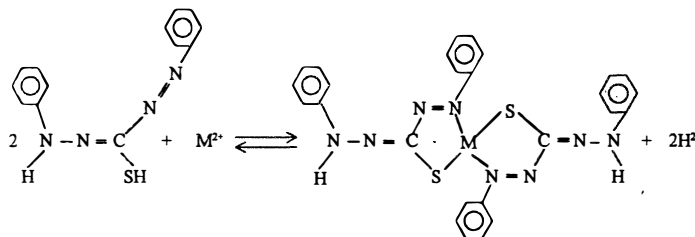


Fig. 1. Equation for the reaction between a metal ion and dithizone ( $M = \text{Pb}$  or  $\text{Zn}$ )

When the reaction is carried out in a separatory funnel, two distinct layers are immediately visible, an aqueous colorless layer and a purple organic layer, which contains the metal-dithizonate complex. In order to determine the concentration of the metal, the complex has to be separated manually and subsequently measured in a spectrophotometer set at 520 nm for lead or 535 nm for zinc. The entire process is quite manageable to a certain point, however, in cases of bulk samples, this is rather cumbersome.

Since its inception in 1975, Flow Injection Analysis (FIA) has introduced fascinating domains in the field of analytical chemistry. The exciting thing about this technique lies in the fact that it can carry out discrete analytical operations in an entirely different manner [5–6]. For instance, solvent extraction can be integrated on-line in a flow injection system to achieve similar results as in the conventional manner, this time with greater ease, efficiency and elegance.

This study therefore concerned (1) the development of a flow injection manifold for the single component determination of lead and zinc in air particulate samples by on-line solvent extraction with diphenylthiocarbazonate, (2) the establishment of the optimum FI conditions with respect to sample volume, reagent concentration and reaction coil length, (3) the characterization of the manifold with respect to detection limit, linear range of detection and precision, and (4) the validation of the FI results by correlating with results from the standard batch method.

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## EXPERIMENTAL

**Instrumentation.** A fabricated flow injection (FI) analyzer was used in this study [7]. This was composed of two sets of five-channel peristaltic pumps, a six-port two-way injection valve and a dual multi-wavelength detector; all housed in a PVC box. The FI system was completed by the addition of a tank of compressed air used to operate the injection valve and a Recorder Company recorder for monitoring the output.

A Shimadzu UV 1201 model was used as an alternative detector for the detection of zinc. The UV 1201 was equipped with a Hellma flow-through cell.

A Milton Roy spectrophotometer was also used for the analysis of the air digests during the batch detection.

An Andersen Ghandivol 2000 portable hi-volume sampler lined with a 10.2-cm diameter Whatman glass microfiber filter was used to collect air samples.

**Reagents.** All reagents were of analytical grade unless otherwise specified, prepared in all-glass distilled water, mixed thoroughly and stored in appropriate reagent bottles.

The dithizone stock solution was prepared by dissolving 0.1 g of diphenylthiocarbazone in 1 L of carbon tetrachloride and was stored in an amber bottle at 20°C. The dithizone working solution was prepared by diluting 10 mL of the dithizone stock solution to 1 L using carbon tetrachloride.

The lead stock solution was prepared by dissolving 0.1 g of lead chloride in 30 mL of water with 1 mL of HCl (1:1), heated to boiling and diluted to 1 L.

The zinc stock solution was prepared by dissolving 0.1 g of 30-mesh zinc metal was dissolved in 1 mL of HCl (1:1), and diluting to 1 L using zinc free water.

**Samples.** Air samples were taken from three sites: Pakna-an, Mandaue City; Colon Street, Cebu City; and, Tagaytay, Cebu City. Two samples were collected per site, each for a period of 1 h at a flow rate of 20 ft<sup>3</sup>/min using a Model G2000P Handi-Vol air sampler lined with a 10.2-cm diameter Whatman glass microfiber filters. The collected samples were stored in a dessicator and weighed to constant weight.

**Sample pretreatment.** Air samples were treated with 30 mL of water and dissolved in 1:1 HCl (using 20 mL per gram of sample), boiled and diluted to 100-mL with distilled water.

**Development of the FI method.** A flow injection manifold was designed based on the study of Gitgano [8]. The FI manifold for lead consisted of four lines corresponding to the acetate buffer at pH 8.5 as carrier, air digests/standard lead solution, carbon tetrachloride and dithizone (Fig. 2). The four lines were pumped simultaneously and allowed to establish a

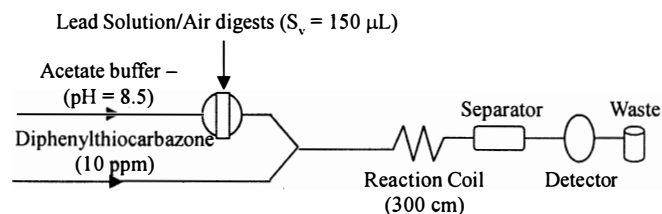


Fig. 2. A schematic diagram of the single component detection of lead by on-line solvent extraction.

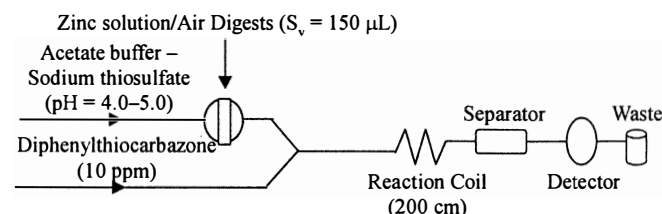


Fig. 3. A schematic diagram of the single component detection of zinc by on-line solvent extraction.

stable baseline. The carrier and the extracting solution were merged and allowed to go through the reaction coil into the separator and towards the detector. The reaction was then activated by injection of the sample into the designed FI manifold whereupon the carrier of acetate buffer solution swept through the sample loop, in effect transporting the sample to a point where it merged with the dithizone solution. This was subsequently followed by on-line complexation, separation and detection.

Figure 3 shows the FI manifold for zinc. An acetate buffer-sodium thiosulfate solution served as the carrier stream that was merged with the dithizone solution and directed to a 200-cm reaction coil and into the separator. The colored complex was then allowed to flow towards the two lower exits of the separator. In order to capture the separated complex from both exits, Teflon tubing of equal lengths were connected and joined together by a T-connector, in effect merging the two solutions before being directed into the detector.

The FI manifolds were optimized with respect to dithizone concentration, reaction coil length and sample volume using the single-factor-at-a-time approach. The optimized manifolds were characterized for its linear range of detection, precision and detection limit.

**Analysis of air samples.** The air digests were analyzed using the developed FI manifolds and the batch methods by external calibration. For all methods, standard metal solutions with varied concentrations ranging from 0.5–50 ppm and dithizone solutions ranging from 10–50 ppm were prepared from the stock solutions. Triplicate analyses were performed.

In the batch method for lead, 10 mL of lead standard solutions were placed in separatory funnels, treated with 10 mL of acetate buffer with pH 8.5, swirled for about 30 sec and mixed with 10 mL of dithizone working solution. The reagents were thoroughly mixed and allowed to separate. The lower organic layer containing the pink dithizonate complex was drawn out and read at 520 nm.

For the batch method for zinc, varied amounts of 1 ppm and 0.1 ppm zinc solutions were placed in a series of separatory funnels. To each solution, 5.0 mL of acetate buffer with pH 4.0–5.0 and 1.0 mL of sodium thiosulfate were added and the mixture was thoroughly mixed. Ten mL of the dithizone working solution was added and shaken for 5 min. The pink zinc-dithizonate layers were placed in cuvettes and read at 535 nm.

In the FI method, the standard metal solutions were simply loaded and injected in the system. After 30–90 seconds, the desired outputs were obtained. Air digests were treated in a similar manner as the standard metal solutions.

## RESULTS AND DISCUSSION

**Development of the FI manifold.** In order to appreciate a flow injection system, it is important to visualize first the conventional extraction scheme. Small portions of the organic solvent containing the complexing agent are added to an accurately measured amount of the analyte in a separatory funnel, shaken vigorously for exactly 5 min, allowed to equilibrate, followed by separation of the aqueous and organic layers. To achieve a good extraction, a fresh amount of solvent is added and a second extraction is carried out. A third, a fourth, or possibly a fifth extraction may follow. In

general, the greater the number of batchwise extractions performed, the more efficient is the separation of the metal complex from the organic solvent.

Figure 4 shows the basic components of a flow injection system where an on-line solvent extraction between sample introduction and detection was installed. Separation of the organic segments from the aqueous segments was achieved by feeding the segmented stream to a fabricated separator [9]. The separator, which is made up of two plates of plexi-glass held together by six sets of screw caps, was made functional by lining it with a semi-permeable hydrophobic Teflon membrane between the two plates (Fig. 5). The segments were introduced in the upper channel and at the interface, the organic segment permeate through the Teflon membrane, into the lower channel and towards the detector.

The carrier solution swept through the sample loop, carrying with it the sample containing the metal. This stream merged with the flowing dithizone solution forming a pink to purple metal-dithizonate complex, which proceeded to the separator. Separation of the organic and aqueous layer was achieved on-line and the colored layer fed to the detector equipped with a flow-through Teflon cell.

**Optimization of the FI manifold.** The optimum response was previously achieved using a 300- $\mu$ L sample size and a 50-mg/L dithizone solution and applied to seawater [8]. Due to some revisions in the manifold, further optimizations with respect to the dithizone concentration, reaction coil length and sample size using the single-factor-at-a-time approach were carried out. The results are shown in Figs. 6–8. The optimized conditions for the FI manifolds for lead and zinc are 150  $\mu$ L sample volume; 10 mg/L dithizone, 200-cm reaction coil for zinc and 300-cm reaction coil for lead. The optimum conditions were nearly the same for both FI manifolds due to the similarities in the chemistry involved, differing only in the pH used for each metal. The FI responses however are quite different.

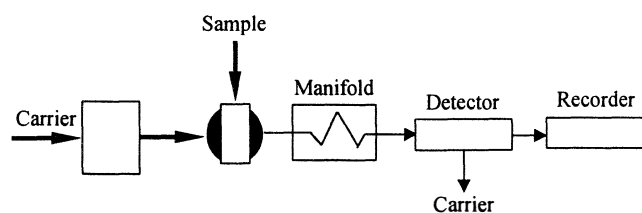


Fig. 4. Basic components of a flow injection system.

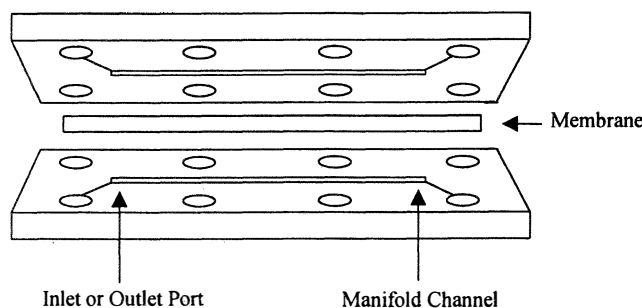


Fig. 5. Schematic diagram of the separator.

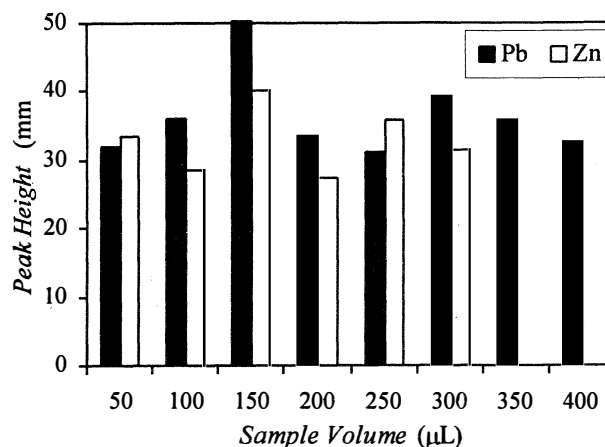


Fig. 6. A graph of sample volume optimization.

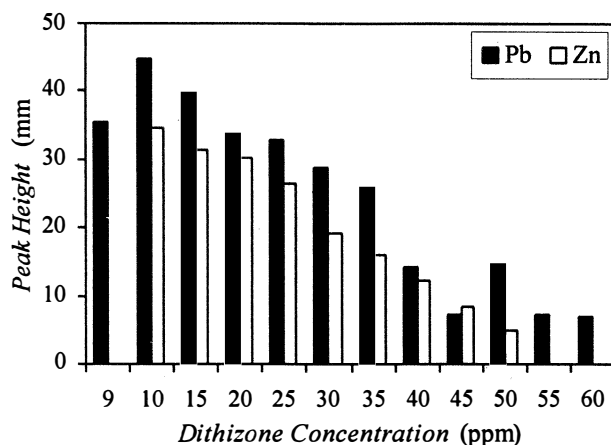


Fig. 7. A graph of dithizone concentration optimization.

**Characterization of the FI manifold.** The optimized FI manifold was characterized according to precision, linear range of detection, response time and detection limits. These four parameters serve as a good scheme to describe a manifold in relation to other FI manifolds previously developed and those existing in literature. Table 1 shows the analytical characteristics of the developed FI manifolds.

The precision of the method was carried out by injecting the standard metal solution five to ten times using the optimized FI manifold. The peak heights were determined and the relative standard deviation (RSD) was calculated. The RSD for both manifolds range from 0.84% to 1.88%, which is comparable to the reproducibility of the expensive atomic absorption spectrometer.

The linear ranges of detection were defined in two levels: one for low-level concentrations (0.5–5.0 ppm) and one for high-level concentrations (10–100 ppm). Both showed good correlation coefficients. The lead manifold had a correlation

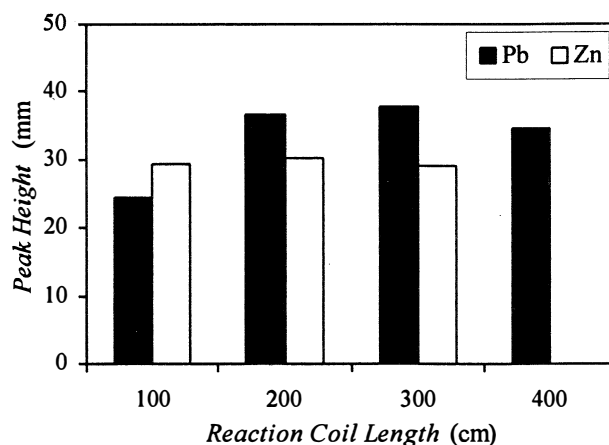


Fig. 8. A graph of the reaction coil length optimization.

coefficient of 0.9995 within the higher range. For zinc, the lower range had 0.9997 and the higher range from 25–100 ppm had 0.9993 correlation coefficients. The two linear ranges make the manifold applicable for the determination of zinc in air as well as in zinc-enriched samples such as highly polluted wastewater, battery mix, paints and corrosion retarders.

The response time was determined by noting the length of time needed to produce an FI response from point of injection to the point of maximum peak development. The minimum response time was found to be 30 sec, which translates to the feasibility of carrying out the analyses of 120 samples/h. The maximum response time of 90 sec corresponded to 40 samples/h.

The experimental detection limit was determined by injecting decreasing concentrations of standard metal solutions. The minimum detectable concentration was 10.00 mg/L using the fabricated mini detector composed of light emitting diodes and photodiodes and 0.5 mg/L using a UV-Vis spectrophotometer as the detector. The improved detection limit using the UV-Vis spectrophotometer was attributed to a high degree of monochromaticity of the light source in the detector. Here, a narrow wavelength of  $535 \text{ nm} \pm 2 \text{ nm}$  can readily be achieved. The use of such detector conforms strictly to Beer's Law, which expresses the direct proportionality of absorbance to concentration only upon conditions of monochromatic radiation. In the fabricated detector, the light sources are light emitting diodes (LEDs), whose radiation output is characterized by a low level of monochromaticity. In particular, the green LED used in this analysis has a wavelength maxima of 565 and a spectral bandwidth of 30–40 nm or greater. Theoretical detection limits based on thrice the standard deviation (3s) are also shown in Table 1. As expected, these values are correspondingly lower and thus would account for the detection of very low levels of metals in air at the ppb and sub-ppb range.

Table 1. Analytical characteristics of the FI manifolds used for the analyses of lead and zinc in air samples.

Parameter	FI Manifold for Lead	FI Manifold for Zinc
Experimental Detection Limit (mg/L)	10 <sup>a</sup>	10 <sup>a</sup> 0.5 <sup>b</sup>
Theoretical Detection Limit (mg/L)	2.03 <sup>a</sup>	0.90 <sup>a</sup> 0.0096 <sup>b</sup>
Precision (% rsd) n = 10 (Pb); n = 5 (Zn)	1.88 <sup>a</sup>	0.84 <sup>a</sup> 1.32 <sup>b</sup>
Response Time(s)	30 <sup>a</sup>	30 <sup>a</sup> 90 <sup>b</sup>
Linear Range of Detection (mg/L)	10–100 <sup>a</sup>	25–100 <sup>a</sup> 0.5–5.0 <sup>b</sup>

a — dual beam multi-wavelength as detector

b — UV-Vis 1201 Spectrophotometer as detector

**Table 2. Comparison of the batch and FI methods for the analysis of lead in air samples.**

Samples	Batch Method ( $\mu\text{g/L}$ )	FI Method ( $\mu\text{g/L}$ )
Paknaan, Mandaue City	$0.446 \pm 0.15$	$0.444 \pm 0.18$
	$0.550 \pm 0.14$	$0.550 \pm 0.17$
Colon Street, Cebu City	$0.534 \pm 0.17$	$0.537 \pm 0.19$
	$0.456 \pm 0.14$	$0.453 \pm 0.18$
Tagaytay, Cebu City	$0.399 \pm 0.19$	$0.408 \pm 0.20$
	$0.383 \pm 0.17$	$0.384 \pm 0.18$

**Table 3. Comparison of the batch and FI methods for the analysis of zinc in air samples**

Sample	Batch Method ( $\mu\text{g/L}$ )	FI Method ( $\mu\text{g/L}$ )
Paknaan, Mandaue City	$3.41 \times 10^{-6} \pm 0.0015$	$2.97 \times 10^{-6} \pm 0.0026$
	$5.16 \times 10^{-6} \pm 0.0015$	$5.53 \times 10^{-6} \pm 0.0025$
Colon Street, Cebu City	$1.15 \times 10^{-5} \pm 0.0029$	$3.74 \times 10^{-6} \pm 0.0029$
	$3.18 \times 10^{-6} \pm 0.0060$	$2.98 \times 10^{-6} \pm 0.0006$
Tagaytay, Cebu City	$1.77 \times 10^{-6} \pm 0.0020$	$1.99 \times 10^{-6} \pm 0.0006$
	$2.24 \times 10^{-6} \pm 0.0015$	$2.48 \times 10^{-6} \pm 0.0010$

**Collection and analysis of the air samples.** Air samples were collected through the G2000P Handi-Vol air sampler in three different sites, each for a period of 1 h. The samples were digested in HCl (1:1) and diluted to 100 mL. The resulting solutions were analyzed by both the batch method and the proposed FI manifold. Results of the analysis of zinc and lead in air are shown in Tables 2–3. The FI manifold for lead highly correlates with the batch method of determination. In the FI manifold for zinc, a slightly lower correlation with the batch is observed. However this does not mean that the manifold fails to meet validation requirements. A closer look at the batch method will show that a number of uncertainties present in the method can be eliminated in the proposed FI method. For instance, the length of shaking during the extraction in the batch method was simplified in the FI process and to a greater extent achieved higher reproducibility compared to the manual shaking and extraction. This uncertainty in the batch is more pronounced when measuring very low levels of metal concentration such as zinc in air. This effect is also seen with the high sensitivity of the UV-Vis spectrophotometer as detector. These observations however are not the same for lead determinations because lead in air was relatively higher than zinc and thus the sensitivity to these uncertainties is greatly minimized.

## ACKNOWLEDGEMENT

The authors express their gratitude to the Department of Chemistry of the University of San Carlos for the provision of materials and equipment and to Mr. and Mrs. Dioscoro Jumamil and family and to Mrs. Natalie Lim-Chio for the accommodation during the sampling.

## REFERENCES

1. Kenkel, J. *Analytical Chemistry: Principles and Techniques*. (Prentice Hall, Inc., 1988).
2. Quirit, L. L. *Kimika* 11, 1 (1995).
3. Vandecasteele, C. and Block, C. B. *Modern Methods for Trace Elements Determination*. (John Wiley and Sons, England, 1993).
4. Spiro, T. and Stigliani, W. *Chemistry of the Environment*. (Prentice Hall, Inc., 1996).
5. Castañares, J.M. *Versatile Manifolds for the Simultaneous Determination of Selected Water Parameters by Flow Injection Analysis*. (Unpublished Doctoral Thesis—University of the Philippines, Diliman, 1995).
6. Ruzicka, J. and Hansen, E. *Flow Injection Analysis*, 2<sup>nd</sup> Ed. (John Wiley and Sons Inc., 1988).
7. Castañares, J. M. *Versatile Manifolds for the Simultaneous Determination of Selected Water Parameters by Flow Injection Analysis*. (Unpublished Doctoral Thesis—University of the Philippines, Diliman, 1995).
8. Gitgano, S. C. *Flow Injection Analysis of Zinc by On-line Solvent Extraction with Diphenylthiocarbazone*. (Unpublished Undergraduate Thesis—University of San Carlos, 1999).
9. Bullezer, E. *Fabricated Separator for On-line Solvent Extraction of Metals by Dithizone*. (Unpublished Data, Maintenance and Calibration Workshop—University of San Carlos, 2000).