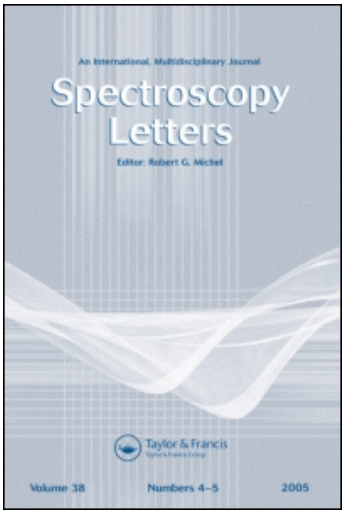

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Determination of Trace Amounts of Zinc in Welding Fumes by Flow-Injection Flame Atomic Absorption Spectrometry

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Abstract: A flow-injection flame atomic absorption spectrometric method for the determination of zinc in welding fumes has been developed. The method is based on the continuous ultrasound-assisted dissolution of the zinc oxide collected on the air filter. Variables such as sonication time, nature and concentration of the acid solution used as dissolving solution, dissolution temperature, flow rate of the continuous manifold, and dissolving solution volume were simultaneously studied by applying a Plackett–Burman design. Results showed that only the concentration of nitric acid solution used as dissolving solution was a statistically significant variable (confidence interval of 95%). Factors such as dissolution temperature and sonication time were finally optimized by using a central composite design. The detection limit was 1.1 $\mu g/m^3$ and the repeatability of the overall method is 1.6% (n = 11) for a zinc concentration of 75.4 $\mu g/m^3$. The proposed method was applied to the determination of zinc in welders' workplace environments.

Keywords: Flame atomic absorption spectrometry, flow injection, welding fumes, zinc

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INTRODUCTION

Zinc may be present as a surface coating on steel products, that is, galvanized steel. The Zn fumes given off during welding of Zn-coated steels consist of zinc oxide.[1] Exposure and inhalation of these fumes causes metal fume fever, a flu-like syndrome common among welders, characterized by acute or subacute symptoms of respiratory tract inflammation, myalgias, and fever.[2,3] These health hazards require not only worker protection but also the need of a regular monitoring of zinc levels in the workplace. Thus, zinc proceeding from welding fumes has been determined by X-ray photoelectron spectroscopy,[4] neutron activation analysis,[5] or X-ray fluorescence spectrometry,[6,7] but atomic absorption spectrometry (AAS) and inductively coupled plasma–atomic emission spectrometry (ICP-AES) have been the analytical techniques more employed for metal determination in welding fumes.[8–13] In fact, the Occupational Safety & Health Administration (OSHA) ID-121, ID-206, and ID-125G methods,[14] National Institute for Occupational Safety and Health (NIOSH) 7300, 7301, and 7303 methods,[15] and National Institute of Security and Hygiene in the Work (INSHT) MTA/MA-025/A92 method[16] for metal and metalloid particulates in workplace atmospheres and metalloid particulates from solder operations are based on AAS or ICP-AES detection.

Sample preparation for analysis of metals in industrial hygiene samples typically involves filter digestion with concentrated mineral acids. However, the use of concentrated nitric or perchloric acid presents several drawbacks including safety precautions. Nowadays, sample dissolution procedures assisted by ultrasonic radiation are an inexpensive, fast, and efficient alternative to traditional sample preparation methods.[17–19] Therefore, intensive treatments with concentrated acids involving filter decomposition can be avoided. Thus, ultrasonic-assisted extraction has been proved as an effective method for discontinuous quantitative extraction of a number of metals from workplace air samples and other analytes in a wide variety of samples.[20,21] Nevertheless, for the determination of metals in air, there are no cases in the literature in which ultrasound energy has been used in a continuous mode coupled to a flow injection system, so for these determinations a complete automatization of the analytical process has not been obtained.

The purpose of the current paper was to develop a fast, simple, and inexpensive method for routine determination of zinc in welding fumes. Flame atomic absorption spectrometry (FAAS) has been considered as an appropriate technique for that purpose, because it is fast, easy to use, sufficiently sensitive to accurately detect trace Zn concentrations, and available in most analytical laboratories. Continuous ultrasound-assisted dissolution of the zinc oxide collected on the air filter is proposed instead of filter digestion, because of the time required, cost, and risks involved in the latter procedure.

MATERIALS AND METHODS

Reagents

Ultrapure water of 18.2 MΩcm resistivity, obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used for the preparation of the reagents and standards. Hydrochloric acid, nitric acid (Merck, Darmstadt, Germany) and 1000 μg/mL zinc standard (Merck) were analytical reagent grade.

Apparatus

A Perkin Elmer Model 5000 atomic absorption spectrometer (Perkin Elmer, Shelton, CT, USA) fitted with a zinc hollow cathode lamp was used. The instrument was set at 213.9 nm. Signals were measured as peak height. The spectrometer output was connected to a Perkin Elmer model 50 servograph recorder with a range of 5 mV. The flow injection system (Fig. 1) comprises a Gilson Minipuls-3 peristaltic pump (Gilson, Villiers Le Bel, France) fitted with Viton tubes, an ultrasonic bath (Selecta, Barcelona, Spain), four Rheodyne injection or switching valves (Rohnert Park, USA), models 5041 and 5301, and a glass minicolumn (100 mm × 3 mm i.d., bed volume 700 μL) (Omnifit, Cambridge, UK). The ends of minicolumn were plugged with filter paper (Whatman 541).

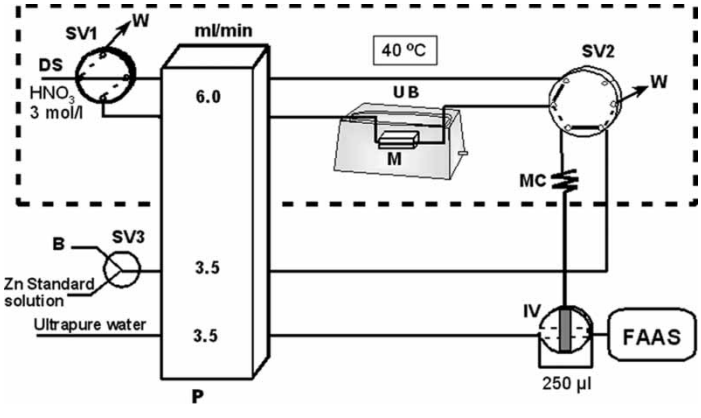

Figure 1. Experimental setup and optimum working conditions for the continuous determination of zinc in welding fumes. DS, dissolving solution; P, peristaltic pump; UB, ultrasonic bath; M, minicolumn containing the filter; IV, injection valve; SV, switching valves; MC, mixing coil; W, waste; B, blank; FAAS, flame atomic absorption spectrometer.

Workplace air samples were pumped with a Gilian HFS-513 air-sampling pump with constant high flow of 750 to 5000 mL/min (Sensidyne, West Cladwell, USA). Welding fumes were collected on Millipore mixed cellulose ester filters (0.8-μm pore size). Each filter is in a polystyrene cassette of 37-mm diameter furnished with a cellulose support.

Statistical analysis of the experimental designs was carried out by means of the Statgraphics Plus V.5.1 statistical package (Manugistic, Inc., Rockville, MD, USA).

Evaluation of the Homogeneity of the Samples

Before starting the optimization study of the continuous dissolution process, the homogeneity of the samples was tested. For this, at the same time were sampled six filters with six air-sampling pumps in a stationary sampling site at the workplace environment placed 0.5 m away from the breathing zone of the welder (in order to not disturb him). The objective was that between sampling filters, variation could not mask the effects of experimental factors to be optimized. With this aim, a set of six filter samples was collected during an effective welding time of 15 min at a sampling flow rate of 1.5 L/min. Zinc oxide particles captured on the cellulose ester filters were analyzed using INSHT MTA/MA-025/A92 method.[16]

Procedure for Zinc Determination in Welding Fumes

The overall arrangement for zinc determination in welding fumes is illustrated in Fig. 1. Each filter was placed into a glass minicolumn (dissolution cell). These dissolution cells were assembled sequentially to the flow system. Once assembled, the dissolution cell was immersed within the ultrasonic bath. Then, by means of a switching valve (SV1), the dissolution circuit was filled with 5 mL of the acid solution (3 mol/L nitric acid). Upon loading the dissolution circuit, SV1 was switched to its other position. Thus, the continuous dissolution system, including the dissolution cell and the peristaltic pump, became a closed circuit. With the aim to dissolve zinc oxide, the acid solution circulated through the dissolution cell at 6 mL/min under ultrasonic irradiation during 4 min. In order to avoid compactness of the filter into the minicolumn and cause overpressure in the flow system during the dissolution step, the direction of the nitric acid flow was changed every 40 s. After the dissolution step, SV2 was switched to its other position, and the dissolved zinc oxide was circulated through the mixing coil where the solution was homogenized. Then, the loop of the injection valve (IV) was filled with a total volume of 250 μL of zinc solution, which was injected into an ultrapure water carrier stream that transported it at 3.5 mL/min to the detector.

Standard solutions containing up to 1.0 μg/mL of zinc in the same acid medium as the dissolving solution (3 mol/L nitric acid) were introduced into the flow system as is shown in Fig. 1.

RESULTS AND DISCUSSION

A multivariate optimization design was applied to study the continuous dissolution step. The variables simultaneously optimized were sonication time, nature and concentration of the acid solution used as dissolving solution (nitric and hydrochloric acid concentrations), dissolution temperature, flow rate of the continuous manifold, and dissolving solution volume. A Plackett–Burman 2 ∧ 6 * 3/16 type III resolution design allowing 6 degrees of freedom involved 12 nonrandomized runs plus one center point was selected for screening study of the behavior of the main factors affecting the continuous dissolution process. The upper and lower values studied for each variable are shown in Table 1. The variable response (% dissolution efficiency) was calculated according to the following equation: % dissolution efficiency = (A/B) x 100, where A is the Zn concentration obtained with the continuous dissolution procedure and B the Zn concentration obtained with the INSHT MTA/MA-025/A92 method.[16] The mean concentration of Zn obtained by the INSHT MTA/MA-025/A92 method was 74.7 μg/m^3 and the relative standard deviation was 2.1%, which is an acceptable value to consider homogeneous the samples obtained with different pumps at the same time. The conclusions of the screening study were that sonication time, dissolution temperature, flow rate of the continuous manifold, dissolving solution volume, and hydrochloric acid concentration

Table 1. Ranges over which the variables were studied and their optimum values

Variable	Low	Upper	Optimum
Plackett–Burman 2 ∧ 6 * 3/16 type III resolution design			
Nitric acid concentration (mol/L)	0	3	3
Hydrochloric acid concentration (mol/L)	0	3	0
Sonication time (min)	0.5	5	—
Dissolution temperature (°C)	20	70	—
Flow rate of the continuous manifold (mL/min)	3	6	6
Dissolving solution volume (mL)	2	5	5
2 ∧ 2 + Star orthogonal central composite design			
Sonication time (min)	4	10	4
Dissolution temperature (°C)	40	70	40

were variables not statistically influential at the 95% confidence level in the ranges studied. Nevertheless, the results showed better % dissolution efficiency with the high value tested for these variables. Though hydrochloric acid concentration has a positive influence, a run of the experimental design achieved a 96.2% dissolution efficiency with the minimum value for this variable (0 mol/L). Thus, this minimum value and high values tested for flow rate of the continuous manifold (6 mL/min) and dissolving solution volume (5 mL) were selected for subsequent experiments. On the other hand, the nitric acid concentration was a factor statistically influential at the 95% confidence level for the dissolution of the target analyte. However, nitric acid concentration was fixed to 3 mol/L because higher acid concentrations can produce serious damage in the spectrometer nebulizer of FAAS, and using this concentration in one of the runs of the Plackett–Burman design a quantitative % dissolution efficiency was achieved (96.2%). Because the Plackett–Burman design only provides the tendencies to the optimum, a new factorial design was performed in order to fine tune the sonication time and dissolution temperature to obtain a quantitative % dissolution efficiency with the minimum values of these variables. For this, we used an orthogonal central composite design, $2 \wedge 2 +$ star with two center points, resulting in 10 nonrandomized runs with 4 error degrees of freedom. Axial distance (α) was selected having a value of 1.07809 in order to establish the orthogonality condition. These experiments were performed keeping all the other factors at optimum values (according to factorial screening design): nitric concentration 3 mol/L, hydrochloric acid concentration 0 mol/L, dissolving solution volume 5 mL, and flow rate of the continuous manifold 6.0 mL/min. The results obtained confirmed that the dissolution temperature and the sonication time were not statistically influential at the 95% confidence level in the ranges studied (40–70°C and 4–10 min, for dissolution temperature and the sonication time, respectively). Figure 2

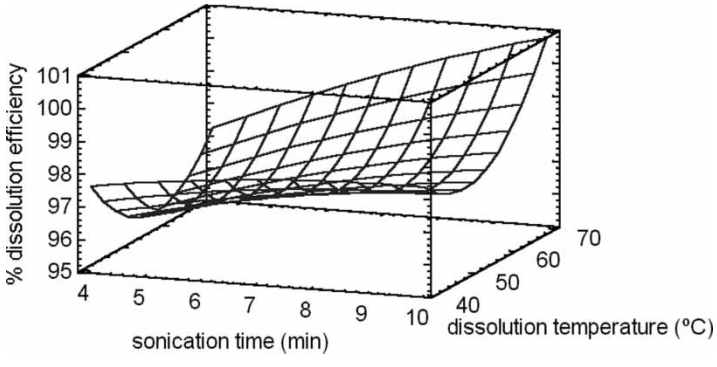

Figure 2. Estimated response surface from the $2 \wedge 2 +$ star orthogonal central composite design.

shows the response surface for this design, which appeared with quantitative % dissolution efficiencies in all the ranges studied for the two variables tested (>95%). Given these findings, in order to increase the sampling frequency, we decided to work with the optimum operational conditions given in Table 1 under the optimum values heading.

Other flow parameters involving zinc determination were also optimized. Thus, it was verified that with a mixing coil length of 500 cm (0.8 mm i.d.), a total homogenization of the acid solution was obtained. Nevertheless, longer lengths would increase the analysis time too much, diminishing the sampling frequency. The carrier flow rate and the injected volume were also studied. The carrier flow rate was studied between 3 and 6 mL/min and the injected volume of the acid solution between 100 and 400 μL. The aspiration flow rate of the nebulizer was adjusted to be the same as the flow rate of the carrier solution. Although the highest aspiration flow rate provides the best sensitivity, at the same time a high dispersion takes place because the carrier flow rate has increased. Therefore, a carrier flow rate of 3.5 mL/min (dispersion equal to 1.1) was chosen as a compromise to obtain the minimum dispersion in the flow system. With regard to the injected volume, it was verified that, as it is logical, when the volume was increased, the sensitivity was increased. Therefore, a volume of 250 μL was chosen, which in addition allows one to inject several times the acid solution, verifying its homogeneity.

In order to test the influence of ultrasound energy on dissolution efficiency, an experiment was developed in absence of ultrasonic radiation. In these conditions, results obtained demonstrated that dissolution efficiency was reduced about 20%.

Analytical Figures of Merit

The calibration graph of the method was run ($n = 7$) under the optimal chemical and flow conditions for the global process. The equation was: absorbance $= 1.9 \times 10^{-4} + 0.23$ [Zn] ($r = 0.9999$; [Zn] = 0 to 1.0 μg/mL). The limit of detection (LOD) based on three times the standard deviation ($n = 30$) of the blank (3 mol/L nitric acid) was found to be 1.1 $\mu g/m^3$ Zn. The relationship between the absorbance signal and the zinc concentration was found to be linear over the range $3.7 - 222.2$ $\mu g/m^3$ for a sampling time of 15 min. The precision of the continuous analytical method was checked for 11 real air samples collected at the same time under the sampling conditions described in the optimization process. The mean $\pm$ standard deviation obtained was 75.4 ± 1.2 $\mu g/m^3$ Zn, which results in a relative standard deviation of 1.6%. The sample throughput of the zinc determination, taking into account the global process, was ca. 11 samples per hour.

Determination of Zinc in Workplace Samples

Three air samples were analyzed by the proposed procedure and another three were analyzed by the INSHT MTA/MA-025/A92 method.[16] Thus, the zinc content found was 146.9 $\pm$ 2.0 $\mu g/m^3$. As the zinc content found by using the reference method is 147.5 $\pm$ 2.8 $\mu g/m^3$, the analytical recovery was 99.6%, which confirms the accuracy of the proposed procedure.

The concentrations of Zn at the workplace investigated (up to 147.5 $\mu g/m^3$) were far below the occupational exposure limit value (VLA) for zinc fumes prescribed by Spanish regulations (5000 $\mu g/m^3$).

CONCLUSIONS

The applied continuous procedure was found to be a reliable and sensitive method for the determination of Zn in welding fumes. The main goals obtained with the proposed method are reduction of sample contamination as well as analyte losses because less manipulation of the sample is required. Furthermore, reagent amounts are reduced, and the sample preparation time is minimized. The method avoids the use of concentrated nitric or/and perchloric acids in a conventional acid digestion procedure; for example, INSHT MTA/MA-025/A92 method requires at least 5 mL of concentrated nitric acid.[16]

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