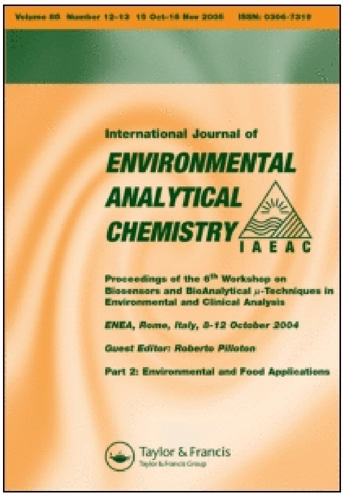

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Application of factorial designs for optimisation of on-line determination of cadmium, lead and nickel in welding fumes by atomic absorption spectrometry

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A flow-injection flame atomic absorption spectrometric method using diluted nitric acid and ultrasound energy to assist metals acid leaching from welding fumes was optimised. Several variables were simultaneously studied by applying a Plackett-Burman design. Results showed that the statistically significant variables (95%) were concentration of nitric acid solution for cadmium, lead and nickel, ultrasonic water-bath temperature for lead and nickel, and sonication time for nickel. Factors such as ultrasonic water-bath temperature and sonication time were finally optimised by using a central composite design. Detection limits were 0.1, 1.0 and 3.4 $\mu g\,m^{-3}$, and repeatability ($n = 11$) were 3.2, 1.9 and 1.6%, for cadmium, lead and nickel, respectively. The proposed method was applied to the determination of cadmium, lead and nickel in welders' workplace environments.

Keywords: flow analysis; cadmium; lead; nickel; acid leaching; air analysis

1. Introduction

Welding is still a common and a highly skilled occupation, but there are several hazardous agents associated with welding processes, among them metallic particulates and their oxides formed by the vaporization and oxidation of metal during the welding process [1]. Welding fume components are harmful to human health. They may be toxic or an irritant to the respiratory system and may cause pulmonary edema, chronic bronchitis, emphysema, pneumonia, asthma, welder's lung and metal fume fever. Furthermore, some of them, for example arsenic, hexavalent chromium, nickel, beryllium and cadmium, exhibit carcinogenic activity [2]. These health hazards require not only worker protection, but also the need for a regular monitoring of trace metals, such as cadmium, lead and nickel, in the workplace air.

The analysis of solid samples, including air sampling filters, in most cases involves using filter digestion with concentrated mineral acids [3–11]. This sample pre-treatment is time consuming and involves some potential drawbacks such as analyte losses and sample contamination, as well as the possibility of systematic errors caused by using strong oxidising acids. Thus, in order to improve the analytical performance for sample

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preparation of industrial hygiene samples such as air filters, ultrasonic metal extraction has been shown to be a realistic alternative to traditional sample pre-treatments. Ultrasound-assisted extraction is an effective way of extracting a number of analytes from different types of samples. The influence of extremely high effective temperatures, which result in increased solubility and diffusivity, and pressures, which favour penetration and transport, at the interface between the extraction solution subjected to ultrasonic energy and a solid matrix, combined with the oxidative energy of radicals created during sonolysis, results in a high extractive power [12–13]. Thus, this methodology has been applied for discontinuous quantitative extraction of a number of metals from workplace air samples and other analytes in a wide variety of samples [14–17]. Furthermore, in comparison with discontinuous procedures, a flow injection (FI) methodology allows repetitive and dynamic exposure of the sample to the extraction solution under ultrasonic radiation. Thus, this dynamic mode minimises sonication times, and as the sample is retained within the extraction cell, avoids the centrifugation and filtration steps to separate the liquid phase, which simplifies the process and increases sample throughput, allowing the possibility of a completely automatic analytical process [18–20]. Nevertheless, for the moment, a completely automatic analytical process based on FI and ultrasound assisted extraction (UAE) has not been proposed for the determination of cadmium, lead and nickel in air.

As many variables are involved throughout the acid extraction process, a multivariate optimisation by using experimental designs is a powerful tool to optimise this procedure. Generally, multivariate optimisation of analytical procedures involves two steps: (1) a preliminary evaluation using a screening design in order to select the variables that have influence on the analytical system, but that does not give the optimum value for each variable; (2) an estimation of the real functional relationship between significant factors and the analytical response (response surface designs), to obtain the optimum values of the variables. Among the different groups of screening designs, Plackett-Burman designs [21] allow us to discover the most significant variables for an analytical system with only a few experiments. In order to obtain the optimum values for each variable involved in the analytical system, central composite designs are the most widely used as response surface designs. These design structures are based on full, or fractional, two-level factorial designs by centre point replication and inclusion of an axial portion [22]. The purpose of the present paper is to develop a fast, simple, and inexpensive method for routine determination of cadmium, lead and nickel in welding fumes. Flame atomic absorption spectrometry (FAAS) has been considered as an appropriate technique for the purpose, because it is fast, easy to use, sufficiently sensitive to detect trace cadmium, lead and nickel concentrations accurately, and available in most analytical laboratories.

2. Experimental

2.1 *Reagents and chemicals*

Ultrapure water of 18.2 $\mathrm{m\,S\,cm^{-1}}$ 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, Germany) and 1000 $\mu\mathrm{g\,mL^{-1}}$ cadmium, lead and nickel standards (Merck, Germany) were analytical reagent grade.

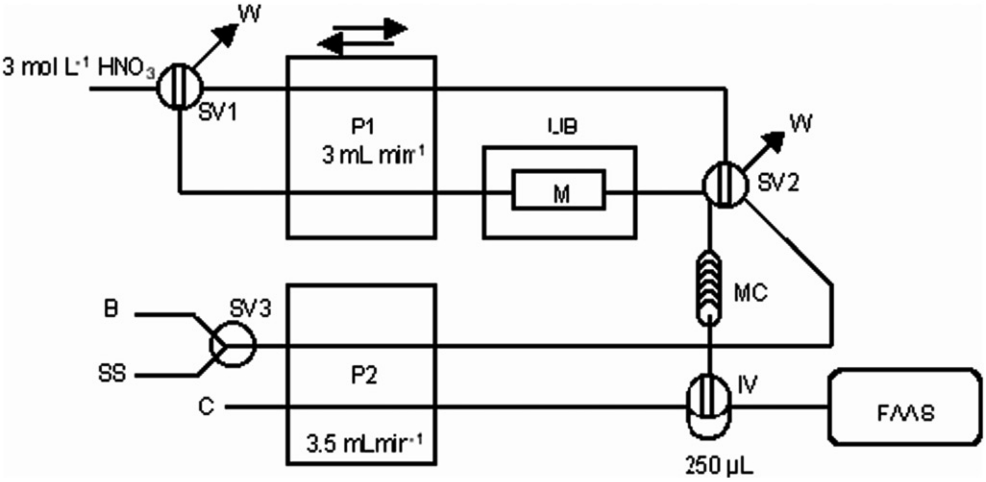

Figure 1. Experimental set-up used for the continuous leaching process and FI determination of cadmium, lead and nickel in welding fumes. P1 and P2, peristaltic pumps; W, waste; UB, ultrasonic bath; M, minicolumn containing the filter; SS, standard solution; B, blank; IV, injection valve; SV1-SV3, switching valves; MC, mixing coil; C, carrier (ultrapure water) and FAAS, flame atomic absorption spectrometer.

2.2 *Apparatus*

A Perkin Elmer Model 5000 atomic absorption spectrometer (Shelton, CT-USA) fitted with hollow cathode lamps was used. The instrument was set at 228.8, 217.0 and 232.0 nm, for Cd, Pb and Ni, respectively. 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 FI system (Figure 1) comprises two Gilson Minipuls-3 peristaltic pumps (Gilson, France) fitted with Viton tubes, an ultrasonic cleaner bath (Selecta, Barcelona, Spain) programmable for temperature and time, and with a frequency of 40 kHz, four Rheodyne injection or switching valves (USA), Models 5041 and 5301 and a glass minicolumn (100 mm × 3 mm i.d., bed volume 700 µL) (Omnifit, UK). The ends of the minicolumn were plugged with filter paper (Whatman 541).

Workplace air samples were pumped with a Gilian HFS-513 air-sampling pump with constant high flow of 750 to 5000 mL min^{-1} (Sensidyne, 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).

2.3 *Reference method*

Open the cassette filter holders and transfer the samples and blanks to clean beakers. Add about 5 mL of concentrated nitric acid, cover the beaker with watch glasses and heated on hotplate (140°C), until the solution is clear. Remove watch glasses and rinse beaker with diluted nitric acid 10% (V/V). Continue heating till semidried (ca. 0.5 mL).

Cool the contents of beaker and diluted 10% nitric acid and transfer the solutions quantitatively to 10 mL volumetric flasks. Subject the solution to a flame atomic absorption spectrometer.

2.4 *Procedure*

Determinations of cadmium, lead and nickel in welding fumes are developed using the approach shown in Figure 1. This dynamic manifold allows the continuous acid extraction of these trace metals and then, their determination by FAAS. The filter is placed within a glass minicolumn (extraction cell of the dynamic UAE system). Then, the extraction cell containing the filter is assembled to the continuous extraction manifold into the ultrasonic bath (preheated to the required temperature, 50, 70 and 80°C, for Cd, Pb and Ni, respectively). The extraction step starts by pumping 2 mL of 3 mol L^{-1} nitric acid. Once loaded the extraction circuit, valve 1 (SV1) is switched to close it. Thus, the continuous extraction system including the extraction unit and the peristaltic pump (P1) became a closed circuit where the acid leaching solution was circulated through the extraction unit at 3 mL min^{-1} under ultrasonic irradiation during 1, 2 or 4 min for quantitative extraction of cadmium, lead and nickel, respectively. During this acid extraction step, the direction of the flow is changed every complete circuit cycle in order to avoid compactness of the sample into the minicolumn that could cause overpressure in the flow system. After extraction, SV2 is switched to allow circulation of the acid extract through the mixing coil. Then, the loop of the injection valve (IV) is filled with a total volume of 250 µL of solution, which is injected into an ultrapure water carrier stream that transport it at 3.5 mL min^{-1} to the detector.

Standard solutions containing up to 2, 20 and 2 µg mL^{-1} for cadmium, lead and nickel, respectively, in the same acid medium as the leaching solution (3 mol L^{-1} nitric acid) are introduced into the flow system as shown in Figure 1.

3. Results and discussion

Nitric and hydrochloric acids were selected as extraction reagents because they are the most frequently used acids for mineralisation, can be obtained in high purity, and lack of the hazards and inconveniences of other acids such as perchloric acid. The main factors affecting the dynamic extraction process were examined. Three factors are related to the acid solution used as leaching solution (two related to its composition : nitric acid concentration and hydrochloric acid concentration, and leaching solution volume), two factors correspond to the ultrasonic stirring (the ultrasonic water-bath temperature and the exposure time to ultrasound) and the flow-rate of the continuous UAE manifold. The effect of changing a factor from a low level to a high level value was examined on a selected response such as percentage extraction efficiency, according to the following equation:% extraction efficiency $= (A/B) \times 100$, where A is the concentration of the metal obtained with the continuous UAE procedure and B the metal concentration obtained with a reference method [5]. The factors and their levels (low and high) are described in Table 1.

3.1 *Plackett-Burman designs*

Plackett-Burman 2ˆ6*3/16 type III resolution designs allowing 6 degrees of freedom involved 12 runs plus one centre point were selected for screening purposes. The upper and

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

				Optimum		
Variable	Key	Low	Upper	Cd	Pb	Ni
Plackett-Burman 2ˆ6*3/16 *design*						
Nitric acid concentration (mol L^{-1})	A	0	3	3	3	3
Hydrochloric acid concentration (mol L^{-1})	B	0	3	0	0	0
Ultrasonic water-bath temperature (°C)	C	20	70	–	–	–
Sonication time (min)	D	0.5	5	–	–	–
Flow-rate of the continuous manifold (mL min^{-1})	E	3	6	3	3	3
Leaching solution volume (mL)	F	2	5	2	2	2
2ˆ2 + *star orthogonal central composite design*						
Ultrasonic water-bath temperature (°C)	C	30	80	50	70	80
Sonication time (min)	D	3	9	1	2	4

lower values studied for each variable are shown in Table 1, and the results of the design expressed as% extraction efficiency are shown in Table 2. Significant effects for each variable and their interactions were checked by analysis of variance (ANOVA) and using the P-value as significance levels, this value expresses how much the probability of a factor is due to the random errors (Table 3). The conclusions of the screening study were that the factors statistically influential at the 95% confidence level on the continuous extraction were nitric acid concentration for cadmium, lead and nickel, ultrasonic water-bath temperature for lead and nickel, and sonication time only for nickel. However, nitric acid concentration was fixed to 3 mol L^{-1} because higher acid concentrations can produce serious damages in the spectrometer nebuliser of FAAS, and using this concentration in one of the runs of the Plackett-Burman designs quantitative % extraction efficiencies were achieved (run 4). On the other hand, the flow-rate of the continuous manifold, acid solution volume and hydrochloric acid concentration and interactions between the variables were not statistically influential at the 95% confidence level within the ranges studied. For all metals, the acid solution volume presents a positive estimated effect, but with low values, and with the aim of increase the analytical sensitivity, the minimum value of this variable was chosen (2 mL). The flow-rate of the continuous manifold has a negative influence on extraction efficiencies, so the minimum value tested (3 mL min^{-1}) was selected for subsequent experiments.

3.2 *Final optimisation by central composite designs*

Having screened out the variables that did not have a significant effect on the response, the two factors sonication time and ultrasonic water-bath temperature were optimised to provide the maximum metal recovery with the minimum values of these variables. For this, we used an orthogonal central composite design, 2ˆ2 + star with two centre points, resulting in 10 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. The results of the design obtained keeping all the other factors at optimum values (Table 1) and expressed as % extraction efficiency are shown in Table 4. These results confirmed that the

Table 2. Design matrix and response values in the Plackett-Burman design (2ˆ6*3/16).

	Key						% extraction efficiency		
Run No.	A	B	C	D	E	F	Cd	Pb	Ni
1	+	−	+	−	−	−	77.3	66.7	50.3
2	+	+	−	+	−	−	74.4	65.1	60.7
3	−	+	+	−	+	−	47.6	66.7	12.3
4	+	−	+	+	−	+	97.5	98.7	95.0
5	+	+	−	+	+	−	95.5	89.4	70.5
6	+	+	+	−	+	+	91.2	86.5	70.5
7	0	0	0	0	0	0	96.5	84.1	40.2
8	−	+	+	+	−	+	62.7	71.7	46.4
9	−	−	+	+	+	−	30.1	19.2	0
10	−	−	−	+	+	+	20.2	0	0
11	+	−	−	−	+	+	65.7	61.3	37.3
12	−	+	−	−	−	+	29.5	21.0	0
13	−	−	−	−	−	−	6.1	0	0

Note: + upper value; − low value; 0 medium value.

Table 3. Estimated effects for each variable and their interactions checked by analysis of variance (ANOVA).

	Cd		Pb		Ni	
Variable	Estimated effects	*P*-values	Estimated effects	*P*-values	Estimated effects	*P*-values
A	54.2083	0.1191	54.1583	0.0911	60.3667	0.0043
B	17.4583	0.4858	20.5083	0.3634	17.4167	0.0481
C	16.5414	0.5061	27.9417	0.2527	22.3833	0.0299
D	17.2083	0.4912	16.1083	0.4560	29.6667	0.0174
E	0.05	0.9961	0.0166667	0.9989	−10.3	0.1760
F	6.38333	0.5434	5.35	0.6610	9.23333	0.2183
A × B	−10.5417	0.6596	−16.2417	0.4528	−5.78333	0.2818
A × C	2.54167	0.9130	−4.50833	0.8214	16.2333	0.0547
A × D	2.60833	0.9108	13.6083	0.5196	12.6167	0.0861
B × C	2.79167	0.8049	15.6417	0.4672	15.8833	0.0570
B × D	−1.19167	0.9591	0.108333	0.9956	7.31667	0.2061
C × D	1.69167	0.9420	2.39167	0.9042	9.73333	0.1334

ultrasonic water-bath temperature and the sonication time were not statistically influential at the 95% confidence level for cadmium extraction in the ranges studied (30–80°C and 3–9 min, for ultrasonic water-bath temperature and the sonication time, respectively). On the other hand, these two variables were statistically influential at the 95% confidence level for lead and nickel extraction. In all the range studied for the sonication time quantitative extraction efficiencies were obtained using a water-bath temperature higher than 30 and 60°C, for Cd and Pb, respectively. In the case of Ni, a quantitative efficiency was obtained if sonication time is longer than 4 min. As interactions between these variables have a positive influence, so that increasing the value of one of them reduces the value of the

Table 4. Design matrix and response values in the central composite design (2ˆ2 + star+).

	Key		% extraction efficiency		
Run No.	C	D	Cd	Pb	Ni
1	0	0	100.0	92.1	94.8
2	28.0478	0	98.7	97.3	100.0
3	81.9522	0	100.0	100.7	79.0
4	−	−	98.7	100.7	79.0
5	0	0	100.0	100.7	87.4
6	0	9.23427	100.0	95.7	89.2
7	−	+	98.7	99.3	71.1
8	+	−	98.7	90.8	79.0
9	+	+	100.0	95.7	73.7
10	0	2.76573	100.0	93.3	58.2

Note: + upper value; − low value; 0 medium value.

other, achieving quantitative extraction efficiencies, and with a goal of increasing sampling frequency, it was proven that it was possible to reduce the sonication time by increasing the water-bath temperature (up to 80°C). Given these findings, we decided to work with the optimum operational conditions given in Table 1.

3.3 *Optimisation of parameters involving the FI system*

Other flow parameters involving cadmium, lead and nickel determination were also optimised. It was proven that a mixing coil length of about 400 cm achieves a total homogenisation of the acid extract, while a longer length would increase the analysis time too much, thus diminishing the sampling frequency. The carrier flow rate and the injected volume were also studied. The carrier flow rate was studied between 3–6 mL min^{-1} and the injected volume of the acid solution between 100–400 μL. The aspiration flow-rate of the nebuliser was adjusted to be the same as the flow-rate of the carrier solution. Although a higher aspiration flow-rate provides better sensitivity, a higher dispersion takes place as the carrier flow-rate increases. Therefore, a carrier flow-rate of 3.5 mL min^{-1} was chosen as a compromise. With regard to the injected volume it was verified that, as is logical, when the volume was increased the sensitivity was increased. Therefore, a volume of 250 μL was chosen, which in addition, permits the acid extract to be injected several times thereby improving its homogeneity.

3.4 *Features of the method*

Calibration graphs were obtained by using peak height as a function of the standard concentrations of cadmium, lead and nickel. Good linearity was obtained up to 3.6 (air volume 135 L), 244.4 (air volume 180 L) and 195.6 (air volume 22.5 L) μg m^{-3} for cadmium, lead and nickel, respectively. The standard addition calibration method was used to investigate the effect of the sample matrix on the analyte absorbance. Thus, the slopes of the standard additions and calibration curves were not statistically different (Student's *t*-test, 95% confidence level), proving the absence of matrix interferences.

Table 5. Analysis of air samples, paired *t*-test and % recovery.

	Proposed method			Reference method					
	Concentration, expressed as mean ± standard deviation $\mu g\,m^{-3}$ ($n = 3$)						% recovery		
Sample	Cd	Pb	Ni	Cd	Pb	Ni	Cd	Pb	Ni
1	0.5 ± 0.0	9.7 ± 0.3	12.4 ± 1.6	0.5 ± 0.0	9.9 ± 1.1	12.9 ± 1.8	100.0	97.9	96.1
2	1.1 ± 0.1	29.2 ± 0.5	62.1 ± 1.5	1.1 ± 0.1	30.6 ± 0.8	65.3 ± 1.6	100.0	95.4	95.1
3	1.7 ± 0.1	42.7 ± 0.8	144.9 ± 2.2	1.8 ± 0.1	44.7 ± 0.8	146.5 ± 2.9	95.0	95.5	98.9
4	1.3 ± 0.1	36.1 ± 0.6	77.3 ± 1.4	1.3 ± 0.1	35.9 ± 0.7	81.5 ± 1.5	100.0	100.5	95.0
5	1.0 ± 0.0	10.0 ± 0.5	46.8 ± 1.5	1.0 ± 0.1	10.4 ± 0.9	46.1 ± 1.7	100.0	96.2	101.5
6	0.7 ± 0.0	9.4 ± 0.4	22.0 ± 1.7	0.7 ± 0.0	9.8 ± 1.1	23.1 ± 1.8	100.0	95.9	95.2

Notes: For Cd: Experimental value of $t = 1.00$; Critical value of t ($n - 1 = 5$, $p = 0.05$) = 2.57.
For Pb: Experimental value of $t = 2.07$; Critical value of t ($n - 1 = 5$, $p = 0.05$) = 2.57.
For Ni: Experimental value of $t = 2.25$; Critical value of t ($n - 1 = 5$, $p = 0.05$) = 2.57.

The detection limits for the three metals calculated based on three times the standard deviation ($n = 30$) of the blank were 0.1, 0.7 and 3.4 $\mu g\,m^{-3}$ for cadmium, lead, and nickel, respectively.

In order to evaluate the precision of the continuous analytical method, the precision was checked for 11 real air samples collected at the same time. Thus, repeatabilities, expressed as relative standard deviation were 3.2% (for a cadmium concentration of 1.7 $\mu g\,m^{-3}$) 1.9% (for a lead concentration of 42.7 $\mu g\,m^{-3}$) and 1.6% (for a nickel concentration of 144.9 $\mu g\,m^{-3}$).

Sample throughputs for cadmium, lead and nickel determinations, taking into account the global process, were ca. 45, 25 and 12 samples per hour, respectively.

3.5 *Analysis of air samples*

The method was applied to determine cadmium, lead and nickel in air samples. Sampling took place in a welding shop and welding fumes were collected during the welding of stainless steel. The results obtained with the proposed method were compared with those achieved by a reference method [5]. To compare the results obtained by both methods, the Paired *t*-Test was applied. As Table 5 shows, both methods do not give significantly different values, thus the agreement between the two methods is satisfactory. Analytical recoveries obtained (shown in Table 5) confirm the accuracy of the proposed procedure.

The concentrations of metals at the workplace investigated, except one for Ni (144.9 $\mu g\,m^{-3}$), were below the occupational exposure limit values (VLA) for cadmium, lead and nickel fumes prescribed by Spanish regulations (2, 150 and 100 $\mu g\,m^{-3}$, respectively).

4. Conclusions

The proposed methodology offers a rapid and efficient sample preparation method for the direct determination of cadmium, lead and nickel in welding fumes. The method avoids the use of concentrated mineral acids and conventional acid digestion procedures to dissolve trace metals from the air filter. Furthermore, diluted nitric acid is used and nitrous vapours formation is reduced. The method offers advantages such as low reagent consumption, minimal sample preparation in a short time, resulting in a high sample throughput, which is important in monitoring occupational pollution, and low wastes.

We have extended the use of ultrasound assisted extraction to the leaching of Cd, Pb and Ni as a prior step to their determination at micrograms per cubic metre levels in welding fumes samples by FAAS, which is an available analytical technique in most laboratories. However, the determination of ultra low levels of these metals is achievable if the method is transferred to ETAAS or ICP-MS equipment.

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