Extraction Procedures for Atomic Absorption Spectrometric Analysis of Toxic Metals in Urban Dust

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A comparison has been made of eight acid extraction systems prior to the atomic absorption analysis of lead, nickel, copper, cadmium, cobalt, chromium, zinc, arsenic and mercury in street dust samples. Statistical treatment of the results enabled a valid comparison to be made in terms of overall extraction efficiency. For the purposes of carrying out large scale environmental surveys it was found that extraction with dilute nitric acid was the most suitable method. Analysis of the extracts by atomic absorption spectroscopy was shown to permit the accumulation of reliable data with the minimum requirement of apparatus and time.

KEY WORDS: Toxic metals, dust, atomic absorption, acid extraction.

INTRODUCTION

Surveys of toxic metal distribution in urban environments have mainly concentrated on lead because of concern about the harmful effects of this metal on the population in general and children in particular. Duggan[1] has assessed the evidence relating lead in street dust to blood lead levels in young children over a ten year period and considers the evidence strong enough to suggest a quantitative relationship between these two parameters. Concern about the harmful effects of lead has encouraged many governments to reduce

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or prohibit the use of lead in petrol as this is thought to be a major source of lead in the environment.

Metals other than lead have also been shown to have harmful effects, particularly on mammalian embryos. These teratogenic effects have been observed in experimental animals at relatively low levels of exposure. Teratology and its possible implications for the human embryo have been reviewed by Earl and Vish,[2] and by Kurzel and Cetrulo.[3] Many of the metals in question occur in significant proportions in street dust, particularly in industrial areas.[4,5]

These considerations have led to a need for the development of analytical techniques which are (a) capable of determining the concentrations of the potentially toxic metals in street dust, and (b) suitable for use in large scale surveys of particular areas. The requirement for such techniques are fairly stringent. They must be sufficiently sensitive for all the metals of interest and because of the large number of such metals and the complex matrix in which they are found, must have a high degree of selectivity. Good precision is a prime requirement for surveys based upon a comparison of results. This is confirmed by Sinex *et al.* who also point out the difficulties in establishing levels of accuracy because of the lack of standard reference materials.[6] A further important requirement is speed of analysis, as many samples need to be analysed to satisfy statistical requirements.

The methods which might be considered include UV absorption spectrophotometry, polarography, anodic stripping voltammetry, inductively coupled plasma spectrometry, X-ray fluorescence and neutron activation analysis. All these methods have particular advantages but in considering analytical suitability together with other important factors such as cost and availability, many workers have settled on atomic absorption spectrophotometry (AAS) as the best compromise. This method will deal with dust samples directly, if used in the flameless mode, but this technique is subject to severe matrix interference as well as being considerably slower than flame AAS. It is possible to aspirate suspensions of powdered solids directly into the flame[7] but this superficially attractive technique has a number of practical disadvantages which lead to results of poor reproducibility. Stupar and Ajlec[8] report coefficients of variation of up to 20% using this method. Conventional flame AAS requires the sample to be in solution. Complete dissolution of dust samples is

possible but requires the use of vigorous acid attack in Teflon lined digestion bombs.[9] In our view such methods are not suitable for large scale surveys, requiring considerable equipment resources, and may be dangerous. Turnbull has reported several explosions using these methods.[10] Extraction methods on the other hand generally involve less hazardous materials under less extreme conditions. Although such methods cannot be expected to extract the whole of each metal in the sample, by subjecting the outer surface of the dust particles to mild acid attack they more closely simulate conditions in the human body.[6] This may be an important consideration if health related problems are being investigated. A major requirement of a partial extraction method is that it should give good sample to sample reproducibility. Several extractants have been suggested by previous workers but these have been employed for only a small number of metals, principally lead.[5,6,11,12,13] Day used 2M nitric acid in studies of the distribution of lead in Manchester[14] and Christchurch,[15] whilst Harrison used 0.07M hydrochloric acid in similar studies in Lancaster.[5]

It would clearly be advantageous in carrying out surveys if a single extractant could be found which extracts as many as possible of the metals which are suspected of having teratogenic effects.[2,3] In this paper we compare the extraction of nine of these metals: lead, nickel, copper, cadmium, cobalt, chromium, zinc, arsenic, and mercury, using eight different extractants. Some of these extractants have been used by previous workers, mainly in connection with the extraction of metals from sewage sludges, sediments and geological materials. In choosing extractant solutions we have been guided by two factors, firstly use in previously reported work and secondly in avoiding chemical problems such as potential precipitations or explosions. We also investigate some of the possible interference effects which might be anticipated in the AAS determination of the metal concentrations in the extractant solutions.

EXPERIMENTAL

Apparatus

An Instrumentation Laboratory Model 251 Double Beam Atomic Absorption Spectrophotometer with background correction was used

for the analysis of arsenic, cadmium cobalt, copper, lead, nickel and zinc in the extracts. The same instrument without background correction was used for the analysis of chromium. For the analysis of arsenic the instrument was fitted with an Instrumentation Laboratory Model 280 hydride kit with signal output to a Bryans 28000 chart recorder.

A Pye Unicam SP90A Atomic Absorption Spectrophotometer fitted with a Shandon Southern Atomic Fluorescence Unit was used for mercury analysis with continuous output to a Pye Unicam SP22 chart recorder.

Reagents

Unless otherwise stated, all reagents were of analytical reagent grade and obtained from Fisons Scientific Apparatus Ltd.

Hydrochloric Acid	S.G. 1.16
Nitric Acid	S.G. 1.42
Nitric Acid	S.G. 1.42 (Primar Grade)
Sulphuric Acid	S.G. 1.84
Perchloric Acid	72% w/w (Standard laboratory reagent grade)
Sodium Borohydride pellets	98% (Aldrich Chemical Co. Ltd.)

Calibration solutions were prepared from Hopkin and Williams "Stan-Ion" solutions (1000 ppm).

Extractant solutions

The composition of the extractant solutions is given in Table I.

Calibration solutions

For all metals except arsenic and mercury six calibration solutions within the ranges given in Table II were prepared in a synthetic background matrix solution.[16] This solution contained metal ions which were not being determined in this study but were present in the sample solutions in significant concentrations. The matrix solution was prepared in 1 M nitric acid and contained six such metals in concentrations similar to those in the sample solutions. The concentrations were as follows: sodium 5 ppm, aluminium

TABLE I

Composition of extractant solutions. (Acids are concentrated (see above) unless otherwise stated.)

Extractant no.	Volume of acid in mixture (ml)				
	Nitric	Hydrochloric	Sulphuric	Perchloric	Ref.
1	50 ml of 2 M				14
2		50 ml of 2 M			
3	50				11
4		50			
5	25	25			19
6	24	24	4		
7	15	6	30		20
8	30		10	10	19

80 ppm, potassium 5 ppm, magnesium 35 ppm, calcium 150 ppm and iron 100 ppm.

For arsenic and mercury, calibration solutions in the range 0.1–0.6 ppm and 0.001–0.006 ppm respectively were prepared in 1 M nitric acid using Primar grade reagent.

Sample collection

A dust sample was collected from a roadside gutter by brushing the dust into a plastic container. After coarse sieving the sample was transferred to a plastic sample bag.

Sample preparation

The sample was dried to constant weight by heating in an oven at 130°C for 48 hours. The dried sample was then sieved through a series of stainless steel sieves of mesh sizes 1 mm, 150 μm and 75 μm. Material finer than 75 μm was retained for further analysis.

Extraction procedure

All glassware was extensively soaked in dilute nitric acid.

Weighed (0.5 g) portions of the prepared dust sample were transferred into 200 ml conical flasks and the sample wetted by not

more than 2 ml of double distilled water. The appropriate acid extractant mixture (Table I) was then added and the flask contents brought to the boil on a hotplate. Gentle boiling was continued for 30 minutes. After cooling, the flask contents were filtered through Whatman GF/D glass fibre filters (previously washed with dilute nitric acid) into 100 ml graduated flasks and diluted to the mark with double distilled water. Duplicate samples and acid blanks were prepared for each extractant.

Instrumental analysis

Instrumental conditions for atomic absorption analysis are shown in Table II.

Background correction was employed for all metals except Cr. A ten degree burner rotation was employed during zinc analysis in order to reduce sensitivity.

The instrument was operated in the 4 sec manual integration mode. For each metal the absorbances of a synthetic background matrix solution blank, calibration standards, acid extraction blanks and sample solutions were recorded in duplicate.

The analysis of arsenic involved a reduction process in which arsenic was reduced to arsine before passing into an argon/hydrogen flame. The reaction flask contained 2 ml of sample solution, 2 ml of hydrochloric acid (S.G. 1.16) and 6 ml of double distilled water. Argon ($31 \, min^{-1}$) and hydrogen ($3.51 \, min^{-1}$) were bubbled through the mixture and passed to the burner. A pellet of sodium

TABLE II

Instrumental conditions for atomic absorption analysis

Element	Flame type	Wavelength (nm)	Band pass (nm)	Concentration range (ppm)
Pb	Air/C_2H_2	283.3	0.5	2–12
Ni	Air/C_2H_2	232.0	0.3	0.2–1.2
Cu	Air/C_2H_2	327.4	0.5	0.5–3.0
Zn	Air/C_2H_2	213.9	1.0	1–6
Cd	Air/C_2H_2	228.8	1.0	0.002–0.12
Co	Air/C_2H_2	240.7	0.5	0.04–0.24
Cr	N_2O/C_2H_2	357.9	0.5	0.2–1.2
As	Ar/H_2	193.7	1.0	0.1–0.6

borohydride was introduced into the reaction flask via a teflon valve. The resulting arsine vapour was passed to the flame where its absorbance was measured and recorded on a chart recorder. During the measurement period the instrument was operated in the 1/4 sec automatic integration mode.

Mercury analysis involved reduction of mercury in the sample solution to mercury vapour using a reducing solution of 10% w/v stannous chloride, 40% v/v hydrochloric acid. 10 ml of this solution and 10 ml of sample solution were mixed in a reaction vessel prior to the analysis and a stream of 3.15 schf of argon was bubbled through the solution to transfer the vapour to a point just below the optical axis of the instrument. The mercury vapour was illuminated by a low pressure mercury lamp placed at right angles to the optical axis. This illumination produced an atomic fluorescence signal which was detected using the emission mode of the instrument and recorded as a peak height on a chart recorder. Traces of mercury in the reducing solution were removed before analysis by passing argon at (0.51 min^{-1}) through 500 ml of the solution for 30 minutes.

Data treatment

Absorbance data and peak height measurements were processed using a Tandy TRS-80 microcomputer. A program was employed which fitted a least squares best fit polynomial to the calibration data up to a maximum of a fifth order polynomial. Metal concentrations were then calculated by interpolation in the extractant solutions and blanks. After correcting for blanks, dilution and sample mass the final results were expressed as μg of extracted metal per gram of dry dust. These results are shown in Table III

Interferences

Atomic absorption spectrophotometry is largely free from spectral interferences but other types of interferences, e.g. chemical, ionisation or background scattering, may occur in solutions with a fairly complicated matrix.

The possibility of interference arising from variations in the iron and sodium concentrations of the extracts was assessed by determining the concentrations of these ions in a typical sample

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TABLE III

Extraction efficiency of acid mixtures. (data in μg of metal extracted per g of sample)

Extractant[a]	Pb	Ni	Cu	Cd	Co	Cr	Zn	As	Hg
1	1942	73.2	345.5	4.5	9.0	59.8	898.8	15.8	1.22
	1921	71.7	348.1	4.4	12.6	57.5	876.5	14.3	1.36
2	1979	59.1	318.0	3.6	12.9	67.7	756.5	15.9	1.34
	1994	58.4	318.1	4.4	13.6	65.4	787.6	16.7	1.79
3	1860	63.8	315.5	3.4	10.3	66.7	789.9	14.1	1.79
	1855	67.4	314.0	3.5	8.8	58.6	778.4	15.5	1.36
4	1941	86.7	329.2	4.3	11.6	67.7	851.3	7.7	2.83
	1945	81.3	324.2	4.3	14.2	68.0	821.9	7.7	2.66
5	1923	59.1	337.9	2.2	15.1	66.2	744.6	19.6	2.19
	1999	65.6	350.4	2.5	16.8	65.4	818.4	17.3	1.91
6	1614	59.6	325.0	2.2	13.9	63.2	757.7	14.3	1.65
	1408	59.8	326.2	2.7	16.6	59.6	735.7	13.7	3.14
7	1438	68.2	297.6	2.3	9.2	76.0	675.4	13.3	1.05
	1381	69.4	285.7	1.7	12.4	76.1	626.0	14.0	1.63
8	492	81.8	367.5	4.6	15.6	92.3	849.8	17.5	0.60
	541	72.1	354.5	4.5	13.5	95.0	787.0	15.1	1.21

[a] see Table I.

Duplicate results are given for each extraction.

solution and then preparing a solution containing a ten fold excess of the same ions. Concentrations of all nine metals in the present study were then determined in the normal and treated solutions. The results are shown in Table IV.

The effects of the excess iron and sodium are small but insignificant in some cases, and in our view justify the use of the' previously mentioned background matrix solution in metal determinations.

Nickel has been reported as causing interference in arsenic determinations by the hydride method.[17] The possibility of interference from this source was assessed by adding a ten fold excess of nickel to a portion of sample solution and comparing it with untreated solution. Identical peak heights were obtained from both solutions.

Interference from these sources did not therefore appear to be a serious problem; however, it was considered wise to use automatic background correction for all elements except chromium.

TABLE IV

Effect of ten fold excess of iron and sodium on metal determinations

Metal	Concentration in normal extract (ppm)	Concentration with excess Fe and Na (ppm)
Pb	8.88	8.70
Ni	0.582	0.563
Cu	1.77	1.77
Zn	4.79	4.72
Cd	0.039	0.032
Co	0.105	0.082
Cr	0.264	0.290
As	0.143	0.151
Hg	0.00289	0.00318

STATISTICAL EVALUATION OF EXTRACTION EFFICIENCY

The replicate results for extraction efficiency are not identical (Table III). For example extractant 1 gives values of 1942 and 1921 ppm for lead. This discrepancy could be explained by a model $x_{ij} = \mu_i + \varepsilon_{ij}$ where x_{ij} is the score of the jth replicate of extractant i for lead, e.g.

$$x_{i11} = 1942, \qquad x_{i42} = 1945$$

μ_i is the mean score that would be obtained by extractant i for lead in the long run (the "true" value). ε_{ij} is the experimental error in the jth replicate of extractant i.

Experimental error does not imply that a mistake has been made or that the measurements have been made carelessly but merely that the results are inevitably affected by factors beyond the experimenter's control, i.e. indeterminate errors.

In analysis of variance the almost universal assumption is that ε is normally distributed, with variance σ^2 where σ^2 is the same for all extractants. In this case there is insufficient evidence to check this effectively but there is no theoretical reason to reject this assumption.

Suppose that for lead, $\mu_1 = \mu_2$. Because of experimental error the mean score of the replicates on extractant 1 and extractant 2 would not be expected to be exactly equal. Thus a small difference between

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the observed means on extractant 1 and extractant 2 would not necessarily mean that μ_1 and μ_2 were different. However, a sufficiently large difference between the observed mean scores could not be explained by experimental error alone and would lead to the conclusion that μ_1 is not equal to μ_2.

Statistical evaluation of the differences in the mean values obtained for each metal using different extractants can be carried out using Duncan's Multiple Range Test.[18] In this test the means obtained for each metal are first arranged in increasing order. Application of the test results in the grouping together of means which cannot be distinguished at the 5% level. The mean values obtained from Table III have been compared in this way and the results are shown in Table V.

The groupings obtained from Duncan's test (Table V) may be used to make comparisons of the overall extraction efficiency of the extractants. For example if Extractant 1 is compared with Extractant 2, then Extractant 1 is better for three metals (Ni, Cu and Zn), equal for five metals (Pb, Cd, As, Co Hg) and worse for one metal (Cr). Extractant 1 would therefore appear to be superior to Extractant 2 overall.

Similar comparisons between extractants lead to an overall ranking order of extraction efficiency. Extractant 8 is generally the most efficient, followed by 4, 1, 5, 2, 6, 3 and 7 in decreasing order.

This ranking order, although statistically valid, tends to obscure some exceptional results for individual metals. Thus Extractant 8 gives an exceptionally low value for lead compared with all other extracts, and similarly Extractant 4 gives a low value for arsenic. It is considered unlikely that these individual discrepancies were caused by gross experimental error as both results are duplicated (Table III) and all lead analyses were carried out at the same time, as were all arsenic analyses.

DISCUSSION

The differences in the weights of a given metal extracted by the different extractants are fairly small (Table III), the range between lowest and highest being typically about 25%. Our preliminary work indicates that more than 95% of lead in street dust is recovered

TABLE V

Application of Duncan's multiple range test to the results shown in Table III

Metal	Extractant no.							
	Mean wt. of metal extracted (ppm)							
Pb	8	7	6	3	1	4	5	2
	516.4	1409	1511	1858	1932	1943	1961	1987
Ni	2	6	5	3	7	1	8	4
	58.8	59.7	62.4	65.6	68.8	72.5	77.0	84.0
Cu	7	3	2	6	4	5	1	8
	291.7	314.8	318.1	325.6	326.7	344.2	346.8	361.0
Cd	7	5	6	3	2	4	1	8
	2.0	2.4	2.5	3.5	4.0	4.3	4.5	4.6
Zn	7	6	2	5	3	8	4	1
	650.7	746.7	772.1	781.5	784.2	817.9	836.6	887.7
As	4	7	6	3	1	8	2	5
	7.7	13.7	14.0	14.8	15.1	16.3	16.3	18.5
Cr	1	6	3	5	2	4	7	8
	58.7	60.9	62.7	65.8	66.6	67.9	76.1	93.7
Co	3	7	1	4	2	8	6	5
	9.6	10.8	10.8	12.9	13.3	14.6	15.3	16.0
Hg	8	1	7	2	3	5	6	4
	0.91	1.29	1.34	1.57	1.58	2.05	2.45	2.75

For each metal the extractants which are underlined in the same group show no significant difference at the 5% level.

using Extractant 1 when compared with a total dissolution method involving the use of aqua-regia/hydrofluoric acid in a Teflon lined pressure bomb.[9] If this high percentage extraction also applies to the other metals then there may be cause for concern about a possible

correlation between the ease of extraction of these metals in our acidic environment and the previously observed efficient solution of metals by gastric juices.[21]

Despite the small differences in the extraction results using the different extractants it has been possible to produce a statistically valid ranking order with Extractants 8, 4 and 1 in the first three places. The statistical treatment tends to obscure the low individual results for lead (Extractant 8) and for arsenic (Extractant 4) which are difficult to explain in chemical terms although Agemian and Chau[11] have commented on the unsuitability of extractants containing sulphuric acid owing to the formation of some insoluble sulphates. In addition the treatment takes no account of other experimental factors which may affect the ability of the analyst to carry out any proposed programme of survey work. One such consideration is the fact that Extractants 8 and 4 are both concentrated acids whereas Extractant 1 is dilute acid. The use of Extractant 1 in preference to the others will reduce the cost of materials as well as improving working conditions for the analyst.

Blank levels were generally very low and within the expected variations in instrumental readings. Although these levels were low in the present work there is always some risk of contamination in a more extended programme, particularly if concentrated acids are employed. This consideration further justifies the use of the dilute acid extraction system.

The levels of precision cannot be assessed statistically from duplicate analyses but we have previously shown relative standard deviations (RSD) in the range 1–3% in a more limited study. Sinex *et al.*[6] consider that RSD values of up to 10% are acceptable in this type of extraction. Whilst not necessarily agreeing with such a wide range we consider that our results for Extractant 1 indicate an acceptable level of precision for most of the metals considered, with the possible exception of cobalt.

Most environmental surveys aim to acquire the largest possible data base in a given time, placing a high priority on speed of analysis even if this involves some slight loss of accuracy and precision. In carrying out such a survey using the dilute nitric acid system (Extractant 1) we have shown that it is possible for one person to analyse forty samples a week for the nine metals considered in the present work. Obviously if some metals,

particularly arsenic and mercury, were omitted this number could be increased.

CONCLUSIONS

In assessing the most suitable extractant for large scale surveys of toxic metals in street dust it is important to consider such factors as safety, ease of preparation, low blank values and low cost as well as extraction efficiency. Our work has led us to the view that the dilute nitric acid extractant (Extractant 1, Table I) is the most consistent with these requirements.

The use of specially purified nitric acid, which is approximately six times the cost of the analytical reagent grade, is not justified as very low blanks are obtained with this latter grade. The cost of materials used in the analysis is thus remarkably low.

We would suggest that low cost surveys, based on the work presented here, would be of considerable help to health authorities in assessing the possible health risks from street dust in specific areas.

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