Comparison of ICP-OES and XRF Performance for Pb and As Analysis in Environmental Soil Samples from Chihuahua City, Mexico

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Research Article

ABSTRACT

Lead (Pb) and arsenic (As) levels on PM_{10} were measured for indoor and outdoor atmospheres and soil samples in Chihuahua City (Chihuahua, Mexico). The concentration of both Pb and As in the soil samples was determined and compared using two instrumental techniques, Inductively coupled-plasma optical emission spectroscopy (ICP-OES) and X-ray fluorescence (XRF). Statistical analyses were performed to determine if significant differences existed between the instrumental techniques, which included F-test for variances evaluation and t-test for mean comparison. The statistical analysis demonstrated that no statistically significant differences were observed for the As concentrations; however, for the Pb concentrations, significant differences did exist between the instrumental techniques. In addition, two microwave assisted digestion techniques were also tested to determine if the difference in the Pb concentrations were due to the extraction technique rather than instrumental method. The first digestion technique used nitric acid (HNO_3), which commonly is used for the extraction of soluble materials within a sample. The second digestion technique used a 1:4 mixture (1 part of concentrated HNO_3: 4 parts of concentrated HCl) which generally extracts more refractory

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elements but destroys more of the sample matrix than HNO_3. Similar statistical tests (F-test and *t*-test) were applied to the data from both digestion types, which showed no significant difference between the extraction techniques.

1. INTRODUCTION

Chihuahua City has a population of approximately one-million inhabitants and is located in the Chihuahuan Desert approximately 235 miles from the US-Mexico border. Currently, Chihuahua is a place with economical activities oriented mainly in the manufacture industry. Nevertheless, the city has historically had a number of industrial activities that are environmentally polluting including an out-of-business metal refinery plant in the southern area, which had been operating for decades producing steel and minerals with heavy elements as lead, zinc, iron, cadmium and others. A byproduct of metal refining/production is the contamination of air sheds and soils with heavy metal pollution. This kind of contamination can sorb to small particulate matter and be transported throughout the city causing pollution problems. Much of the sorption in the environment occurs on particulate matter smaller than 10 µm (PM_{10}), the range of sizes that affect the human respiratory system most persistently at the alveolar levels (Wagner and Travis, 1996). Although several institutions have begun studies about the incidence of particulate matter and other airborne pollutants in public health, only few reports have been published to date. Furthermore, these studies did not consider environmental differences found in diverse settings like open spaces in private residents and backyards that could affect the human exposure to several pollutants. Based on the lack of information about environmental levels of hazardous elements, the Department of Chemistry of the University of Texas at El Paso (UTEP), the Environmental Science and Engineering, and the Environmental Science Department of the Advanced Materials Research Center (CIMAV, for the acronym in Spanish) in Chihuahua City started research to compare the levels of lead (Pb) and arsenic (As) in airborne particulate matter and in soil dust from different environments: inside of chosen households in a high-polluted area of the city, outside of the same property (front and backyards), and the general outdoors around an atmospheric sampling station property of CIMAV. Pb and As concentrations were measured and recorded for indoor and outdoor atmospheres and soil samples for comparison purposes. The studies began in the spring of 2006 and were concluded in the winter of 2007.

Benin *et al.,* in 1995, did a study on the concentrations of As, Cd and Pb in the street dust of Chihuahua City. Their findings revealed potentially hazard concentrations of Pb in soils as well as in children, with an average of 32 and 277 mg/kg of arsenic and lead, respectively. This study was the first time that airborne particulate matter and soil analyses were presented in a single study on Chihuahua. Duane *et al.* (1996) did a comparison between graphite furnace atomic absorption spectroscopy (GFAAS), ICP-MS (inductively-coupled plasma with mass spectrometry), ICP-AES (inductively-coupled plasma with atomic emission spectroscopy) and energy dispersive X-ray fluorescence (EDXRF) in polluted soils in the former Democratic Republic of Germany. This study showed that the destructive chemical analysis does not always provide the correct result due to incomplete leaching of the sample in the acid digestion process. Thus the reported concentrations obtained by ICP are commonly lower than the absolute concentrations in a sample. However, this incomplete

leaching is not present in X-ray fluorescent techniques because acid leaching is not used. However, other problems do exist with XRF, such as in homogenous samples, which leads to higher error in the statistics of the collected data. Comparisons between several analytical techniques, such as ICP-MS, XRF, and graphite furnace atomic absorption spectroscopy (GFAAS) have been utilized for the characterization of ultrapure materials such as tellurium, quartz, and copper. These studies show that chemical leaching methods provide the highest sensitivity (Balaram *et al.*, 2005). Djingova *et al.* (1998) evaluated the comparative performance of neutron activation analysis (INAA), EDXRF, ICP-AES and atomic absorption spectroscopy (AAS) in the analysis of trace metals in plants. This study showed the detection limit and accuracy of INAA and GFAAS were superior to the other techniques investigated. The interesting issue in this study is that they report limitations in the use of ICP-AES for toxic elements monitoring, finding that some of detection limits, particularly for As, cobalt (Co), cadmium (Cd), nickel (Ni), antimony (Sb), and Pb were too high, especially when the solution has a high acid concentration. Pyle *et* al. (1996) found that XRF offer similar results compared to ICP-AES or FAAS for soil samples (Pyle *et al.,* 1996). Singh *et al.* (2006) used a comparison between ICP-AES, ICP-MS and XRF to characterize elephant ivory finding advantages in every methodology depending on the element measured. Marina *et al.* (2001) used XRF and ICP-AES to determine phosphorus in raw materials and ceramics, and found similar results between both methods. Nevertheless, XRF was the preferred mode of analysis based on better sensitivity and ease of sample preparation. Hannaker *et al.* (1984) reports a close agreement with XRF and ICP-AES for a large number of elements over a wide concentration range, for major and minor constituents in geological materials.

In the current study, PM_{10} samples from indoor and outdoor environments from Chihuahua City were evaluated for Pb and As concentrations. The study involved the collection of the particulate matter soil samples, acid extraction of these samples followed by the determination of the Pb and As concentrations. In addition, two extraction techniques were performed for a comparison of the extraction/leaching of the elements of concern from the samples. These microwave-assisted extraction techniques used either concentrated nitric acid (HNO_3) or a mixture of HNO_3 and HCl, in 1:4 ratio for elemental extraction. In addition, two analytical instrumental techniques, XRF and ICP-OES, were investigated to compare the concentrations of Pb and As in the samples.

2. EXPERIMENTAL DETAILS

2.1 SAMPLING SITES

A fixed atmospheric sampling point designated by CIMAV was selected as a geographical center and a 2 km radius was designated for the sampling site. The sampling area can be described as a semi-urban geographical region in the southern zone of the city, with high-traffic use streets, Lombardo Toledano Avenue. Eight soil samples randomly-selected were collected for XRF/ICP-OES analysis, and another 3 were used for HNO_3 and HNO_3- HCl leaching/extraction. Subsequently the data were compared as described below.

2.2 SAMPLING METHODS AND SAMPLE PREPARATION

Eight composite soil samples were obtained from the different geographical points (see the map in the Figure 1). The samples (approximately 0.5-1 kg each) were conditioned for 24 hours in a silica-gel dessicator, mixed manually, then ground and sieved to achieve a

homogenous sample with a 200 mesh particle diameter (75 µm). Subsequently, three 0.25 g replicates of the homogenized samples were weighed for digestion and another 0.25 g of each sample was utilized for XRF analysis.
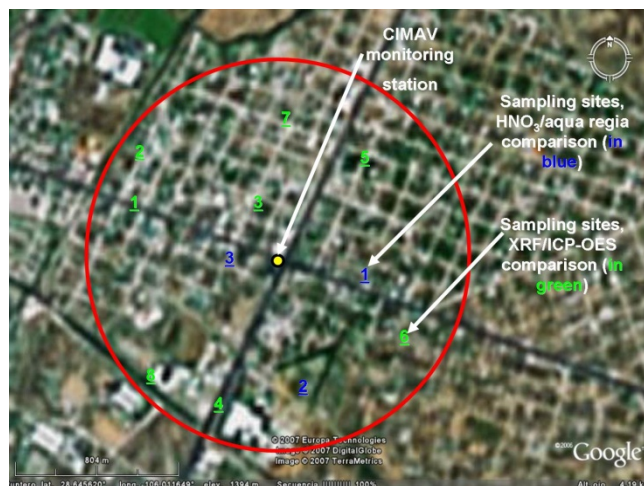

Fig. 1. Sampling zone for XRF/ICP-OES and HNO$_3$/HNO$_3$-HCl study

2.3 ANALYTICAL PROCEDURES

The weighed samples (0.25 g) were digested using a CEM Mars X Microwave digestion system (CEM Corp., Matthews, NC, USA). The conditions of the microwave digestion were: a power of 1200 W, temperature of 150°C, time of 35 minutes (EPA IO-3.1 and EPA IO-3.4; USEPA 1999a and 1999b), volume of 5 mL of HNO$_3$ or 5 mL of HNO$_3$-HCl. The digests were filtered and stored in plastic vials, for analysis by ICP-OES. Elemental standards were prepared for the range of 0.1, 0.5, 1, 5 and 10 parts per million (ppm) with deionized water as a blank. The ICP-OES equipment used was a Perkin Elmer ICP-Optical Emission Spectrometer Optima 4300 DV with 1500 W of RF Power (Perkin Elmer Inc., Sheldon, CT, USA), peristaltic pump flow rate of 1.5 mL/min and gas flows of 15 L/min for the plasma, 0.2 L/min for the auxiliary flow and 0.65 L/min for the nebulizer. A 30 second washing time was performed between each sample. The wavelengths used for analysis of Pb and As were 220.353 nm and 197.197, respectively.

In addition, the samples were also analyzed using a Fischerscope X-Ray XDAL High Performance Energy Dispersive X-ray Fluorescence (EDXRF) apparatus (Fischer Inc., Enskededalen, Sweden). The concentration was measured by counting the pulses of energy dispersed at the different energy levels. The XRF setup was as follows: multichannel silicon pin diode detector, a tungsten x-ray source set at a voltage of 50 keV, an aluminum filter was used in every measurement, a collimator of 0.6 mm, a counting time of 60 seconds, and three replicates per sample were recorded. In addition, to verify the results and to calibrate the instrument, the following standards from the National Institute of Standards and Technology (NIST) were utilized: SRM 2586 (Trace Elements in Soil, As: 8.7 +/- 1.5 ppm, Pb: 432 +/- 17 ppm), SRM 2587 (Trace Elements in Soil, As: 13.7 +/- 2.3 ppm, Pb: 3242 +/- 57 ppm), SRM 2710 (Montana I Soil, As: 626 +/- 38 ppm, Pb: 5532 +/- 80 ppm) and SRM 2711 (Montana II Soil, As: 105 +/- 8 ppm, Pb: 1162 +/- 31 ppm).

2.4   DATA ANALYSIS

Pb/As Concentration Calculations with XRF Results

Pb and As are two elements that can be correlated by the dispersion of X-Ray energy since both share one of the main lines of dispersion in the EDXRF spectra ($Pb_{L\alpha}$ and $As_{K\beta}$ are at the same energy). The area under the peak for $Pb_{L\alpha}$&$As_{K\beta}$ (between 10.15 keV and 10.87 keV) and $Pb_{L\beta}$ energy (between 12.21 keV and 13.03 keV) was measured. A calibration curve from the NIST standards was performed and a linear correlation between concentration and counts/s second was obtained.

As:
$$y = 139.53 - 21.633x \qquad (1)$$

Where
y = Energy area ratio for ($Pb_{L\alpha}$&$As_{K\beta}$ line)/$As_{K\beta}$
x = Concentration of As, ppm

Pb:
$$y = 0.00512x \qquad (2)$$

Where
Y = Energy area ratio for $Pb_{L\alpha}$&$As_{K\beta}$ line
X = Concentration of Pb $Pb_{L\alpha}$&$As_{K\beta}$ line>

2.5 HNO$_3$/HNO$_3$-HCl DIGESTIONS PERFORMANCE COMPARISON

A comparison of means between the results obtained with HNO$_3$ and HNO$_3$-HCl digestion for Pb and As was performed using paired-data test differences (Tables 1 and 2) and a two-tailed *t*-test (Tables 3 and 4). The t_{table} range of acceptance of null hypothesis (H$_0$) and the t_{calc} was calculated with Microsoft® Office Excel 2003 statistical tools within the criteria of the 95% confidence interval and two tails, for both elements (Pb and As). We assume as a null and alternate (H$_1$) hypothesis:

$$H_0 : \mu_1 = \mu_2$$

$$(3)$$

$$H_1 : \mu_1 \neq \mu_2$$

$$(4)$$

where the μ is the mean of the compared data from both techniques, and SE is the standard error for the same data. Minitab® ver. 15 and Microsoft® Office Excel 2003 statistical software were used for the calculations.

An ANOVA with F_{table} and F_{calc} (F is the Fisher statistical parameter that use the variances of each factor to know if exist differences between two different populations) was performed using the same statistical software with α = 0.025, showing the results for Pb and As in Tables 5 and 6 respectively, and comparing 3 different factors: sample, method and the interaction between the sample and method. If the $F_{calc} < F_{table}$ then both extraction techniques have similar results.

2.6 COMPARISON OF THE PERFORMANCE OF XRF/ICP-OES ANALYTICAL TECHNIQUES

A comparison between XRF and ICP-OES analytical techniques was performed using the same statistical tools utilized in the digestion techniques comparison. Variances and means between ICP-OES and XRF methods were calculated with the paired-data test (Tables 7 and 8), a two-tailed *t*-test (Tables 9 and 10) and ANOVA (Tables 11 and 12), for 8 random samples (3 replicates per sample), with the Pb and As results. F-test and *t*-test were calculated for the data of both elements and both techniques, with a confidence interval of 95% assuming the same null and alternate hypothesis for *t*-tests performed on the samples used for the digestion comparison.

3. RESULTS AND DISCUSSION

3.1 COMPARISON OF HNO3/HNO3-HCI DIGESTION

A comparison between two different digestion methods was conducted to determine if a real difference in the concentrations of Pb and As exists when using HNO_3 or HNO_3-HCl for microwave assisted digestion. The 3 samples were digested with 3 replicates using both HNO_3 and HNO_3-HCl in two different batches using the same microwave equipment conditions. Results for Pb are shown in Tables 1, 3 and 5 and the results for As are shown in Tables 2, 4 and 6.

In Tables 1 and 2, a comparison between the results of HNO_3 and HNO_3-HCl digestions is shown for Pb and As, respectively. A paired-data test is practiced subtracting the concentration value obtained using the HNO_3-HCl as a digestion reagent from the value obtained from digestion of the sample using HNO_3 alone, in every sampling point. One interesting thing is that the standard deviation (STDDEV) for As paired test is lower than in the case of Pb, indicating more accuracy in the values obtained for As than in the Pb values. This kind of test is practiced to determine the mean and the standard error (SE) and calculate the t_{calc}. The comparison of t_{calc} and t_{table} permitted us to know if the H_0 is accepted or rejected (if $t_{calc} < t_{table}$, H_0 is accepted; if $t_{calc} > t_{table}$, H_0 is rejected). For both Pb and As, in this case, H_0 is accepted, showing that does not exist any statistical difference between the use of HNO_3 alone or HNO_3-HCl in the microwave-assisted digestion system.

The t_{calc} value are inside the range of acceptance for both elements (Tables 3 and 4), failing to reject the null hypothesis ($H_0 : \mu_1 = \mu_2$). The means of both methods of digestion are very similar at a probability level of 5%; meaning that the differences between the results from both digestion techniques are negligible. Using the same controlled conditions and apparatus, we expected that the analytical results would not be statistically different between the two digestion methods.

Table 1. Means comparison for the extraction of Lead

Sample	HNO$_3$	HNO$_3$/HCl	Average	Average	Std. dev.	Std. dev.	Pooled Std. dev.	T calc	T table
1	22.3	23.73	20.31333	23.54333	1.865083	1.20093	1.569	2.059	2.776
1	20.04	24.64							
1	18.6	22.26							
2	40.3	39.97	40.51667	40.44333	2.033675	1.334516	1.720	0.043	2.776
2	42.65	41.95							
2	38.6	39.41							
3	43.54	42.72	43.07	42.27667	4.603032	2.841062	3.825	0.207	2.776
3	47.42	39.24							
3	38.25	44.87							

Degrees of freedom = n1+n2 -2 =4 confidence at the 95%

Table 2. Means comparison for the extraction of Arsenic

Sample	HNO$_3$	HNO$_3$/HCl	Average	Average	Std. dev.	Std. dev.	Pooled Std. dev.	T calc	T table
1	2.05	3.05	2.633333	2.796667	0.641275	0.648254	0.645	0.253	2.776
1	3.32	3.28							
1	2.53	2.06							
2	4.49	5.27	4.903333	5	0.673078	0.242693	0.506	0.191	2.776
2	5.68	4.93							
2	4.54	4.8							
3	4.03	4.42	3.91	4.97	0.461844	0.477598	0.470	2.256	2.776
3	4.3	5.21							
3	3.4	5.28							

Degrees of freedom = n1+n2 -2 =4 confidence at the 95%

Table 3. t-test for Pb in two digestion techniques

t-TEST FOR Pb RESULTS IN TWO DIGESTION TECHNIQUES		
Ho: The average of the mean differences for both techniques is zero		
H_1: The average of the mean differences is more than or less than zero		
t_{calc} =	Mean/SE	0.52577088
t_{table}		2.36
t_{calc} is inside the acceptance range for H_0, so H_0 is accepted		

Table 4. t-test for As in two digestion techniques

t-TEST FOR As RESULTS IN TWO DIGESTION TECHNIQUES		
Ho: The average of the mean differences for both techniques is zero		
H_1: The average of the mean differences is more than or less than zero		
t_{calc} =	Mean/SE	1.53871787
t_{table}		2.36
t_{calc} is inside the acceptance range for H_0, so H_0 is accepted		
There is no difference between digestion techniques.		

As can be observed in Tables 5 and 6, there exists differences between the values of every sample. This is an expected behavior, since the sampling sites were randomly selected (does not exist any relation between the sampling points). It does not exist a statistical difference between the two digestion methods for both elements, so both chemical reagents (HNO_3 and HNO_3-HCl) can be used to extract Pb and As from the samples used in this study. Also, the interaction between the sampling and digestion methods was not significant, so the study demonstrates the capacity of the digestion system with the already measured parameters (sample and method comparison separately).

Hassan *et al.* (2007), modifying several parameters from the EPA Method 3051 for microwave acid digestion of heavy metals, tried to improve the recoveries for many elements in soil, dust and sediments. They determined that the addition of HCl to the HNO_3 acid used for the digestion did not result in any significant variations in the recovery for almost all the elements tested (Pb included) with the exceptions of As and Zn (As and Zn had better recovery with the HCl addition). When compared to HNO_3 alone, nevertheless, the improvement in the As recovery was compensated by the interferences caused by the chlorine ion (Cl^{-1}) in the final sample matrix.

Table 5. ANOVA results for Pb in HNO_3 and HNO_3-HCl digestions comparison

Source	SS	Df	MSS	F_{calc}	F_{table}
Factor 1 (Samples)	1558.66	2	779.33	116.62	3.89
Factor 2 (Methods)	2.79	1	2.79	0.42	4.75
Interaction	13.81	2	6.90	1.03	3.89
Error	80.19	12	6.68		
Total	1655.46	17			

Conclusions:

Samples: F_{calc} =116.62 > F_{table} = 3.89, exist differences in Pb levels

Methods: F_{calc} = 0.42 < F_{table} = 4.75, does not exist differences in Pb levels

Interaction: F_{calc} = 1.03 < F_{table} = 3.89, interaction effects between locations and methods do not exist.

According to Sandroni and Smith (2002), 6 ml of pure HNO_3 was found to be the optimum acid mixture for microwave-assisted digestion of several heavy metals (including Pb) in sewage sludge and some soils. We use a similar quantity in our samples in our own method (5 ml) and obtained a similar result. This quantity of acid was the most advantageous combining good recovery of the elements with less dangerous operation and less reagent cost.

Table 6. ANOVA results for As in HNO_3 and HNO_3-HCl digestions comparison

Source	SS	Df	MSS	F_{calc}	F_{table}
Factor 1 (Samples)	1558.66	2	779.33	116.62	3.89
Factor 2 (Methods)	2.79	1	2.79	0.42	4.75
Interaction	13.81	2	6.90	1.03	3.89
Error	80.19	12	6.68		
Total	1655.46	17			

Conclusions:

Samples: F_{calc} =116.62 > F_{table} = 3.89, exist differences in As levels

Methods: F_{calc} = 0.42 < F_{table} = 4.75, does not exist differences in As levels

Interaction: F_{calc} = 1.03 < F_{table} = 3.89, there is no interaction between locations and methods

3.2 COMPARISON OF THE ICP-OES/XRF RESULTS

The paired-data test (Table 7) and *t*-test (Table 9) for Pb show a disparity between the values obtained from the different analytical methods. F_{calc} for these conditions was out of the tabulated range (Table 11), thus a rejection of the null hypothesis occurs. This result demonstrates that variances from both instrumental techniques were statistically different. Under the assumption that the variances of both instrumental techniques are not independent, a new paired-data testing is calculated to determine if the means from the two techniques are the same. The results from this test showed that the t_{calc} is out of the range of t_{table}, rejecting the null hypothesis and proving that both methods have different means and generate different results. In almost all the replicates (with the exception of two, from the same sample, Table 7) the ICP-OES values for Pb were much lower than in the same sample using XRF determination by a ratio of approximately 1:3. This result is explained by the digestion methodology. The EPA method used in this study is only a digestion technique and not a total extraction technique (Hassan *et al.*, 2007). This digestion method only recovers Pb that is easily soluble and not structurally contained Pb. The procedure to obtain full Pb content in a soil sample is much more complex and uses toxic chemicals such as HF (Tessier *et al.*, 1979; Mahan *et al.*, 1987). Bingol *et al.* (2005) showed the differences between the concentrations of XRF technique and FAAS for fly-ash from a power plant, where Pb had a concentration rate of approximately 4:1 for XRF:FAAS. In this study, a different digestion procedure was performed using a mixture of HNO_3, HF, and $HClO_4$; obtaining an increased concentration ratio of almost 8:1 for XRF:FAAS rather than if a softer digestion procedure (1% w/w HCl and different levels of HF) is used.

In the opposite case, paired-data test (Table 8), *t*-test (Table 10) and ANOVA (Table 12) shown that both XRF and ICP-OES methods fail to reject the null hypothesis for As (Table 10), proving that both techniques have the same variances and means. The As results are very interesting since it is a difficult element to quantify with other spectroscopic techniques. These results show that the XRF technique is a good choice for As measurements in soil.

As can be seen in Tables 11 and 12, there were differences between the Pb and As values in every sample. This is an expected behavior, since the sampling sites were randomly selected (does not exist any relationship between the sampling points). In the comparison of analytical techniques case (XRF and ICP-OES), does not exist a statistical difference between the two methods for As (Table 12), but the opposite occurs for Pb (Table 11). This means that we can use both equipments to analyze adequately the As, but the ICP-OES apparatus was more accurate and precise than XRF in this conditions and for this concentrations. There was no interaction between the statistical values measured for the samples and the values from the method in the case of Pb, but this occurred for the As. This is interesting since it would be important to establish that certain type of samples are most adequate for As measurements with ICP-OES and another kind of samples for XRF analysis. This can be for the volatility of As depending of the sample and lab conditions.

Table 7. Paired-data test between the results of ICP-OES and XRF techniques for Pb

Locations	Pb (mg/kg) by		PAIRED TEST DIFFERENCES
	ICP	**XRF**	
1	73.74	171.09	-97.35
1	49.12	191.21	-142.09
1	46.02	179.69	-133.67
2	24.68	244.14	-219.46
2	42.66	244.14	-201.48
2	30.46	220.70	-190.24
3	58.47	257.81	-199.34
3	98.17	259.77	-161.60
3	50.85	244.14	-193.29
4	222.72	341.80	-119.08
4	382.60	513.67	-131.07
4	231.40	259.77	-28.37
5	52.36	210.94	-158.58
5	104.72	240.23	-135.51
5	55.20	222.66	-167.46
6	132.99	312.50	-179.51
6	274.40	312.50	-38.10
6	145.66	236.33	-90.67
7	268.26	382.81	-114.55
7	273.10	255.86	17.24
7	474.83	365.23	109.60
8	168.58	300.78	-132.20
8	277.53	310.55	-33.02
8	185.31	302.73	-117.42
		MEAN	-119.05
		STD. DEV.	77.72
		SE	16.20633703

Rasmussen *et al.* (2005) reported that EDXRF detection limits are satisfactory for the major and minor elements, but not sufficient for trace and ultratrace elements, thus, proposing the use of ICP-MS for analysis of trace and ultratrace elements. They compared the values obtained for some metals present in airborne particulate matter sampled using glass fiber filters from a MiniVol™ system and analyzed with a Perkin Elmer ICP-MS and a Kevex 771 EDXRF. The chemical analysis methodology chosen was very similar to the EPA 3051 methodology (NIOSH 7300, for the analysis of elements, Pb and As included, by ICP); with the only difference being the digestion reagent of 1 ml of $HClO_4$ and 4 ml of HNO_3 instead of the 10 ml of HNO_3 reported by the EPA method. Even with this reagent change, the National Institute for Occupational Safety and Health (NIOSH) technique has the same drawbacks as the EPA procedure. This is because they are not extractive procedures and only recover the elements present in the first layers of the particulate matter. This made the comparison of EDXRF and ICP-MS results more complicated because the XRF techniques penetrates deeper into the sample bonds than the chemical extraction procedure for ICP-OES, showing higher concentrations for the same sample. The soil and particulate matter matrices possess

the elements of interest (Pb and As) in concentrations high enough for the XRF detection limits. Public health concerns and the environmental levels are much higher than a few micrograms per kilogram of Pb or As, high enough to be detected by almost all the modern analytical apparatus.

Table 8. Paired-data test between the results of ICP-OES and XRF techniques for As

Location	As (mg/kg) by		PAIRED TEST
	ICP	XRF	DIFFERENCES
1	14.94	12.16	2.78
1	10.08	10.24	-0.16
1	12.88	10.48	2.40
2	2.41	8.27	-5.86
2	2.58	9.89	-7.31
2	4.16	10.23	-6.07
3	5.31	5.37	-0.06
3	12.03	1.36	10.67
3	4.71	1.38	3.33
4	1.41	16.26	-14.85
4	7.42	6.58	0.84
4	3.45	15.89	-12.44
5	5.07	0.00	5.07
5	12.58	0.00	12.58
5	5.80	0.00	5.80
6	11.11	0.00	11.11
6	28.19	0.00	28.19
6	13.67	0.00	13.67
7	9.79	17.46	-7.67
7	10.61	15.49	-4.89
7	21.48	17.52	3.95
8	10.10	2.28	7.82
8	18.99	4.50	14.49
8	9.92	14.12	-4.20
		MEAN	2.47
		STD. DEV.	9.79
		SE	2.040493114

Table 9: t-test for Pb in XRF/ICP-OES comparison

t-TEST FOR Pb RESULTS IN TWO ANALYTICALTECHNIQUES

Ho: The average of the mean differences for both analytical techniques is zero

H_1: The average of the mean differences for both
analytical techniques is different from zero

t_{calc} =	Mean/SE	7.34595011
t_{table}		2.07

t_{calc} is out of the acceptance range for H_0, so H_0 is rejected

The analytical techniques produced different results

Table 10. t-test for As in XRF/ICP-OES comparison

t-TEST FOR As RESULTS IN TWO ANALYTICALTECHNIQUES

Ho: The average of the mean differences for both analytical techniques is zero

H_1: The average of the mean differences for both
analytical techniques is different from zero

t_{calc} =	Mean/SE	1.208371
t_{table}		2.07

t_{calc} is inside the acceptance range for Ho, so Ho is accepted

Both analytical techniques produced similar results

Table 11. ANOVA results for Pb in ICP-OES and XRF comparison

Source	SS	Df	MSS	F_{calc}	F_{table}
Factor 1 (Samples)	314476.10	7.00	44925.16	12.52	2.31
Factor 2 (Methods)	170077.53	1.00	170077.53	47.38	4.15
Interaction	44188.77	7.00	6312.68	1.76	2.31
Error	114857.75	32.00	3589.30		
Total	643600.14	47.00			

Conclusions:

Samples: F_{calc} = 12.52 > F_{table} = 2.31, there were differences in Pb levels between samples.
Methods: F_{calc} = 47.38 > F_{table} = 4.15, the analytical techniques produced different results.
Interaction: F_{calc} = 1.46 < F_{table} = 3.89, there is no interaction between samples and analytical technique.

Table 12. ANOVA results for As in ICP-OES and XRF comparison

Source	SS	Df	MSS	F_{calc}	F_{table}
Factor 1 (Samples)	591.03	7.00	84.43	4.78	2.31
Factor 2 (Methods)	72.97	1.00	72.97	4.13	4.15
Interaction	768.17	7.00	109.74	6.21	2.31
Error	565.50	32.00	17.67		
Total	1997.66	47.00			

Conclusions:

Samples: F_{calc} = 4.78 > F_{table} = 2.31, the As levels among samples were different

Methods: F_{calc} = 4.13 < F_{table} = 4.15, the analytical techniques were similar

Interaction: F_{calc} = 6.21 > F_{table} = 2.31, at least in one case there was interaction between the analytical technique and the sample.

4. CONCLUSION

This study indicates that the HNO_3 and HNO_3-HCl digestion methods have no significant difference in the extraction of Pb and As from soil samples. In addition, the comparison of XRF and ICP-OES analytical techniques showed no significant statistical difference in the analysis of As. However, Pb determinations showed that ICP-OES and XRF had significant differences between the concentrations determined by each instrumental technique. Nevertheless, these differences are more than likely in the digestion/extraction methodology which comes down to the total and the extractable concentrations in a soil sample. Similar results were found in the literature. Under the same conditions, the addition of HCl to the HNO_3 used for the acid digestion of the samples caused no variations in the elemental recovery for Pb and As in several environmental matrix such as soil, dust, and sediments. The use of HNO_3 alone, in almost the same quantity of our research has been reported as optimum for Pb recovery and even better for As (although this recovery improvement is compensated with the Cl^- interferences). Other reports established that the detection limits of several kind of XRF apparatus are not good enough for trace elements (Pb and As included), but the environmental concentrations of Pb and As are much higher than the trace values.

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