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Determination of Lead, Chromium, Manganese and Zinc in Slurries of Botanical and Biological Samples by Electrothermal Atomic Absorption Spectrometry Using Tungsten-Containing Chemical Modifiers

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Abstract. Lead, Cr, Mn and Zn in slurries of botanic and biological samples were determined by electrothermal atomic absorption spectrometry (ETAAS) using W, Ir, $NH_4H_2PO_4$, W and $NH_4H_2PO_4$, Ir and $NH_4H_2PO_4$, W and Ir, and $W + Ir + NH_4H_2PO_4$ chemical modifiers in an 0.2% (v/v) Triton X-100 plus 0.2% (v/v) nitric acid mixture. Zeeman effect background correction was performed and platforms inserted into graphite tubes were used. Comprehensive comparative studies were carried out with respect to pyrolysis and atomization temperatures, atomization and background absorption profiles, characteristic masses, detection limits and accuracy of the determinations in the presence and absence of modifiers. The mixture of $W + Ir + NH_4H_2PO_4$ was found to be preferable for the determination of Pb, Cr, Mn and Zn in slurry samples. The pyrolysis temperatures of the analytes were increased up to 1250 °C for Pb, 1000 °C for Zn, 1400 °C for Cr and Mn by using $W + Ir + NH_4H_2PO_4$ with an 0.2% (v/v) Triton X-100 plus 0.2% (v/v) nitric acid mixture used as diluent solution. The optimum masses of the mixed modifier components were found to be 20 μg W + 4 μg Ir + 50 μg $NH_4H_2PO_4$. The characteristic masses of Pb, Cr, Mn and Zn obtained are 16.3, 5.6, 0.1 and 1.1 pg, respectively. The detection limits of Pb, Cr, Mn and Zn based on integrated absorbance for 0.5% (m v^{-1}) slurries were found to be 0.14, 0.06, 0.02 and 0.01 μg g^{-1}, respectively. The slurries of botanic and biological certified and standard reference materials were analyzed with and without the modifiers. Depending on the sample type, the percent recoveries increased from 63 up to 104% for analytes when using the proposed modifier mixture.

Key words: Botanic and biological slurries; ETAAS; matrix modification; lead; chromium; zinc.

Determination of trace, toxic or essential elements such as Pb, Cr, Mn and Zn in botanic and biological samples is important and of great interest due to human exposure and environmental parameters [1–7]. Electrothermal atomic absorption spectrometry (ETAAS) is one of the most frequently employed techniques for the determination of trace amounts of elements present in different samples due to its high sensitivity, selectivity and simplicity [1–10]. Difficulties occurring with ETAAS include high background absorption and interference effects of constituents in the sample matrix. Different atomization techniques using different atomization surfaces, different background correction methods, such as deuterium lamp and Zeeman effect, and different chemical modifiers have been used to improve the precision, to lower the detection limit or to

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decrease matrix interferences in the determination of analytes such as Pb, Cr, Mn and Zn in various samples [1–12].

The aim of using a modifier in ETAAS is to increase the thermal stability of analytes so that higher pyrolysis temperatures can be used to volatilize the higher matrix components and to decrease background signals of real samples [2, 3, 6, 13]. Different chemical modifiers such as W [6–8, 10, 14–16], Ir [8, 16–18] and ammonium dihydrogen phosphate [19–21] are used to stabilize analyte elements. Platforms inserted into pyrolytically coated graphite tubes and Zeeman effect background correction are also favorable and essential for analyte determinations in samples. The slurry sampling technique has been extensively employed for the analysis of biological and inorganic samples in order to simplify sample preparation and to avoid some inconveniences related to wet decomposition and dry ashing procedures [5–7, 10, 22].

In this study, the thermal stabilizing effects of W, Ir, $NH_4H_2PO_4$, W and $NH_4H_2PO_4$, Ir and $NH_4H_2PO_4$, W and Ir and $W + Ir + NH_4H_2PO_4$ single and mixed chemical modifiers in an 0.2% (v/v) Triton X-100 plus 0.2% (v/v) nitric acid mixture used as diluent on the determination of Pb, Cr, Mn and Zn in slurries of botanic and biological certified and standard reference materials by ETAAS were comprehensively examined. The $W + Ir + NH_4H_2PO_4$ modifier mixture in an 0.2% (v/v) Triton X-100 plus 0.2% (v/v) nitric acid mixture has so far not been studied. The effects of mass and mass ratio of modifiers on the analyte absorbance values, pyrolysis and atomization temperatures of analytes in sample solutions were investigated. Atomization and background profiles, characteristic masses (m_o) and limits of detection (LOD) of the analytes obtained were compared in the presence and absence of modifiers. Lead, Cr, Mn and Zn in slurries of botanic and biological samples were determined in the presence of the proposed $W + Ir + NH_4H_2PO_4$ modifier mixture and in the absence of a modifier in order to verify the accuracy and precision of the method.

Experimental

Instrumentation

A Hitachi Model 180/80 atomic absorption spectrometer equipped with a 180/78 graphite furnace, a Zeeman effect background corrector, and an automatic data processing unit (180/205) was used for all Pb, Cr, Mn and Zn absorption measurements. Hitachi pyrolytic graphite coated graphite tubes (P/N-190/6007) containing graphite platforms (P/N-190/6008) were employed throughout the experiment. Lead, Cr, Mn (Hitachi) and Zn (Photron, Australia) hollow cathode lamps were used as radiation sources. Instrumental parameters and operating conditions for analytes were used as recommended by the manufacturer unless otherwise stated. A 20 µL volume of calibration or sample solution together with modifier solution was injected into the platform by means of an autosampler (P/N-170/126). All absorbance signal measurements were carried out using the integrated absorbance (peak area) mode. Argon (99.995%, w/w) was used as the purge gas and interrupted during atomization. A Varian Model 9176 recorder was used in a 20 mV/FS span in order to obtain atomization and background signal profiles. The optimized graphite furnace operating conditions and temperature program for the determination of Pb, Cr, Mn and Zn are summarized in Table 1.

Table 1. Heating program for Pb, Cr, Mn and Zn determination in sample digests with different modifiers

Step	Temperature (°C)	Ramp (s)	Hold (s)	Ar flow rate (mL min^{-1})
Dry-1	50–130	30	–	250
Dry-2	130–300	20	10	250
Pyrolysis	200-Variable[a]	30	20	250
Atomization	Variable[b]	0	5	0
Cleaning	Variable[c]	0	3	250

[a] See Table 2; [b] Optimum atomization temperatures are 2000 °C for Pb and Zn, 2700 °C for Cr, and 2500 °C for Mn, respectively; [c] Cleaning temperatures used are 2650 °C for Pb and Zn, and 2800 °C for Cr and Mn, respectively.

Reagents and Standards

Ultrapure water (resistivity 18 MΩ cm) from an ultrapure water system (Nanopure Infinity, Barnstead, P/N-1161, Dubuque) was used in the preparation of all solutions. All acids and reagents were of analytical grade. Nitric acid 65% (w/w), HCl 37% (w/w), H_2O_2 35% (w/w) from Merck (Darmstadt, Germany) were used to dissolve the samples and for dilution. All solutions prepared were stored in high-density polypropylene bottles. Plastic bottles, autosampler cups and glassware materials were cleaned by soaking in 20% (v/v) HNO_3 for two days, rinsing four times with ultra-pure water, and drying. Autosampler washing solution containing 0.2% (v/v) HNO_3 plus 0.2% (v/v) Triton X-100 was used to avoid clogging of the autosampler sampling capillary tip and to improve the dispersion of sample solution onto the platform [7, 23].

Standard solutions (2.0 g L^{-1}) of W and Ir were prepared from 200 mg W powder (Eimer and Amed) dissolved in 30% H_2O_2 and 234 mg IrO_2 (Merck, Germany) in 10% HNO_3 solution, diluted to 100 mL with ultra-pure water after evaporation of acids. The 4.0% $NH_4H_2PO_4$ (Merck, 99.99% pure) was prepared by dissolving 4.0 g of $NH_4H_2PO_4$ in a sufficient volume of ultra-pure water, transferring into a 100 mL volumetric flask and diluting to the mark.

Stock standard solutions of Pb, Cr, Mn and Zn (1.0 g L^{-1}) obtained from BDH Chemicals (Poole, UK) were used. Calibration solutions of analytes were freshly prepared by successive dilution of the stock standard solutions to the desired concentrations in 0.2% (v/v) nitric acid solution.

Reference Materials

Tomato leaves (1573a), pine needles (1575), spinach leaves (1570a), bovine liver (1577b) and bone ash (1400) standard

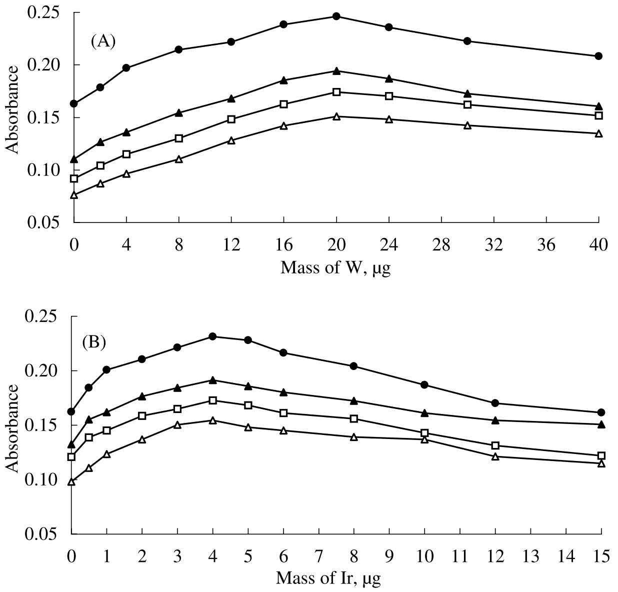

Fig. 1. Effect of mass of (A) W with fixed 4 µg of Ir and (B) Ir with fixed 20 µg of W modifier mixture on the absorbance values of Pb (△) in CRM 155 (38.5 $\mu g\,L^{-1}$), Cr (●) in CRM V 10 (16.4 $\mu g\,L^{-1}$), Mn (▲) in SRM 1577b (4.52 ± 0.73 $\mu g\,L^{-1}$) and Zn (□) in SRM 1573a (2.78 ± 0.06 $\mu g\,L^{-1}$) sample solutions, respectively

reference materials (SRMs) from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA), and hay powder (V-10), freeze dried animal blood (A-13), whey powder (155) and cotton cellulose (V-9) certified reference materials (CRMs) from International the Atomic Energy Agency (IAEA, Vienna Austria) were used to check the accuracy and precision of the proposed method.

Slurry Preparation

Slurries of samples were prepared by accurately weighing 0.05–1.0 g of the sample in Teflon vessels with covers. A 4 mL mixture of 2% (v/v) HNO_3 plus 1% (v/v) H_2O_2 (1:1) and 1 mL 0.2% (v/v) Triton X-100 was added to each sample before setting them aside overnight (room temperature) [6, 7, 10, 24–26]. After stirring with a PTFE-coated magnetic bar for 5 min [7], the resulting slurry was homogenized in an ultrasonic bath (Branson 3200, USA) for 30 min in order to break up particle agglomerates [6, 7, 10, 24, 25]. The slurries were transferred into acid-cleaned 10 or 25 mL glass calibrated flasks and diluted to the mark with diluent after washing the interior surface of the Teflon vessel three times. Blank solution was prepared according to the procedure mentioned above. For each sample, three slurries were prepared. All measurements were carried out for at least eight replicates after transferring the slurries into acid-cleaned propylene autosampler cups.

Analytical Procedure

Sample solutions diluted with 0.2% (v/v) nitric acid plus 0.2% (v/v) Triton X-100 were used to obtain the optimum parameters for determinations of Pb, Cr, Mn and Zn by ETAAS. A 1 mL sample solution with a sufficient concentration of analyte was mixed with 1 mL of modifier solution (2.0 $g\,L^{-1}$ W, 0.4 $g\,L^{-1}$ Ir, 2.0 $g\,L^{-1}$ W and 0.4 $g\,L^{-1}$ Ir or 2.0 $g\,L^{-1}$ W + 0.4 $g\,L^{-1}$ Ir + 5.0 $g\,L^{-1}$ $NH_4H_2PO_4$). 20 µL of sample solution together with single or mixed modifier solutions or without a modifier was injected into the platform inserted into the pyrolytic graphite-coated tube. The absorbance versus mass or mass ratio of modifier curves obtained for the analytes in slurry samples using the optimized temperature program given in Table 1 are given in Fig. 1. The optimum atomization and maximum pyrolysis temperatures for the analytes obtained with and without the modifiers are given in Tables 1 and 2.

Results and Discussion

Modifiers

Lead and Zn are volatile elements that are lost from the graphite atomizer at temperatures higher than 500 °C (Pb) and 400 °C (Zn), respectively in the absence of a modifier [27]. The main purpose of using a modifier is to increase the thermal stability of the analyte elements, and to decrease the matrix effects and background signals, allowing their determinations in real samples without loss of analyte mass [6, 14, 20]. Temperature conditions such as ramp and hold times, pyrolysis and atomization temperatures given in Tables 1 and 2, and atomization/background profiles of analytes in slurry samples with and without a modifier

Table 2. Maximum pyrolysis temperatures, characteristic masses and detection limits of Pb, Cr, Mn and Zn obtained with and without modifiers (diluting factor of 200 $mL\,g^{-1}$)

Modifier	Pyrolysis temperatures (°C)				m_o (pg)				LOD ($\mu g\,g^{-1}$)			
	Pb	Cr	Mn	Zn	Pb	Cr	Mn	Zn	Pb	Cr	Mn	Zn
Without	850	950	1000	450	52.1	24.8	3.6	7.3	1.53	1.06	0.14	0.08
$NH_4H_2PO_4$	900	1000	1050	650	46.3	21.3	2.2	5.9	1.18	0.87	0.13	0.05
W	950	1200	1200	850	39.7	19.6	1.7	4.7	0.93	0.75	0.09	0.04
Ir	1000	1200	1150	850	34.8	18.4	1.4	4.1	0.75	0.66	0.07	0.03
W + $NH_4H_2PO_4$	1100	1300	1300	900	29.4	12.8	0.8	3.4	0.48	0.43	0.06	0.02
Ir + $NH_4H_2PO_4$	1050	1300	1250	900	26.6	9.1	0.5	2.9	0.45	0.28	0.05	0.02
W + Ir	1200	1350	1350	950	19.7	7.3	0.3	1.8	0.30	0.13	0.03	0.01
W + Ir + $NH_4H_2PO_4$	1250	1400	1400	1000	16.3	5.6	0.1	1.1	0.14	0.06	0.02	0.01

solution were roughly investigated in some preliminary experiments in order to find the optimum ETAAS conditions.

The effect of mass and mass ratio of W and Ir on the pyrolysis temperatures and absorbance values of analytes in CRM 155 (Pb content is 38.5 µg L^{-1}), CRM V-10 (Cr content is 16.4 µg L^{-1}), SRM 1577b (Mn content is 4.52 ± 0.72 µg L^{-1}) and in SRM 1573a (Zn content is 2.78 ± 0.06 µg L^{-1}) slurry samples were studied and are given in Fig. 1. As can be seen, the optimum mass and mass ratio of the components were found to be 20 µg for W, 4 µg for Ir and 20 µg W/4 µg Ir. The optimum mass of $NH_4H_2PO_4$ (50 µg) found in previous studies [20] was used together with a W + Ir modifier mixture for analytes. The mass values of W and Ir found were compared with those reported in previous papers [28, 29], and similar results were observed.

The pyrolysis and atomization temperatures of analytes in SRM 1400 (Pb content is 49.0 ± 0.7 µg L^{-1}), in SRM 1570a (Mn content is 5.31 ± 0.31 µg L^{-1}) and SRM 1577b (Zn content is 2.78 ± 0.06 µg L^{-1}) slurry sample solutions in the absence and presence of modifiers were investigated. The atomization and pyrolysis temperatures of analytes found with and without modifiers are also given in Tables 1 and 2. As can be seen in Table 2, the pyrolysis temperatures of analytes obtained with W + Ir + $NH_4H_2PO_4$ are higher than those obtained with single or mixed modifier components or without a modifier. The pyrolysis temperatures of analytes with the W + Ir + $NH_4H_2PO_4$ modifier mixture were compared with previous studies [14, 20, 27, 29], and similar results were observed. Small differences in temperatures may be dependent on the instrumental parameters and different tubes or platforms used. As can be seen in Table 2, pyrolysis temperatures of analytes with W + Ir + $NH_4H_2PO_4$ are higher than W and Ir because of the additional effect of $NH_4H_2PO_4$. The pyrolysis temperatures of analytes are also higher in the presence of $NH_4H_2PO_4$ and diluent. Generally, NH_4^+, PO_4^{3-}, NO_3^- and Triton X-100 have proved to eliminate interferences in samples and to be efficient in reducing the modifiers and analytes to dispersed and reactive metallic forms at higher temperatures [9, 20]. The optimum atomization temperatures allow complete atomization of the analytes in samples [30]. Atomization temperatures of analytes were obtained by keeping the pyrolysis temperatures constant in the presence and absence of modifiers.

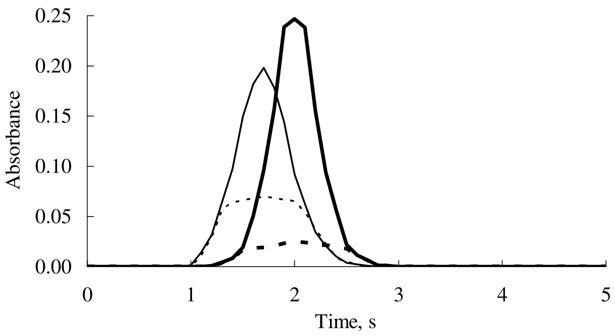

Fig. 2. Atomization and background profiles of Cr in CRM V-10 (Cr content 16.4 µg L^{-1}) obtained without (—, - - - -) and with a 20 µg W + 4 µg Ir + 50 µg $NH_4H_2PO_4$ (▬, ••••) modifier mixture

Atomization and background signals of Pb, Cr, Mn and Zn in slurry sample solutions in the presence and absence of modifiers were compared in order to show how the modifier affects the absorbance profiles of the analytes [20, 31]. Figure 2 shows the analyte and background atomization profiles of Cr in CRM V-10 (Cr content is 16.4 µg L^{-1}) without and with W + Ir + $NH_4H_2PO_4$ as an example. As can be seen, when W + Ir + $NH_4H_2PO_4$ modifier mixture is used, higher atomization and lower background signals are obtained, and the signal/noise ratios of the analytes are higher than in the absence of the modifier. Although the appearance times of the atomic analyte signals are the same, the maximum peak times were observed to have shifted to a later time when W + Ir + $NH_4H_2PO_4$ modifier mixture was used.

Analytical Characteristics

Lead, Cr, Mn and Zn in slurry samples were determined in the presence and absence of modifiers by means of the calibration graph method. Calibration graphs were constructed against aqueous standard solutions, with a linear range extending up to 80 µg L^{-1} for Pb, 25 µg L^{-1} for Cr, 8 µg L^{-1} for Mn and 3 µg L^{-1} for Zn, respectively. The volume of aqueous standard solution or sample solution together with and without a modifier injected into the platform was 20 µL. The calibration graphs obtained were linear, and all correlation coefficients (r) for the analytes were higher than 0.99.

The characteristic mass (m_o = mass of analyte corresponding to 0.0044 abs. units) and limits of detection (LOD, $3\sigma_B$) are important parameters with respect to the sensitivity of the proposed method and might be influenced by instrumental parameters [20, 31, 32]. The characteristic masses and detection limits of the analytes were determined with and without the modifiers from 20 consecutive measurements of the blank solutions [33, 34] for an 0.5% ($\mathrm{m\,v^{-1}}$) slurry concentration. The results found are given in Table 2. As can be seen, better m_o values and the lowest detection limits were obtained with $W + Ir + NH_4H_2PO_4$ in diluent solution, and they are similar to the results obtained in previous studies [4, 8, 20, 22, 31]. Slight inconsistencies in results may be due to the instrumental and operating parameters used.

Based on the results obtained, $W + Ir + NH_4H_2PO_4$ modifier mixture in 0.2% (v/v) Triton X-100 plus 0.2% (v/v) nitric acid mixture was proposed for Pb, Cr, Mn and Zn determinations in slurries of botanic and biological samples. This can promote analyte stabilization on the platform, increase the sensitivity and lower the detection limit associated with higher pyrolysis temperatures [8].

Analysis of Reference Materials

Nine reference materials were analyzed using the slurry method employing the proposed $W + Ir + NH_4H_2PO_4$ in diluent in the absence of a modifier to test the accuracy and performance of the method. The heating program (Table 1), pyrolysis temperatures of analytes (Table 2), optimum mass and mass ratio of modifiers and the integrated absorbance mode were used. In all cases the calibration was run against aqueous standard solutions with and without modifiers in diluent solution. The results obtained with and without the $W + Ir + NH_4H_2PO_4$ modifier mixture are given in Table 3. They are presented as the average ± confidence interval (T student value = 2.365, 7 degrees of freedom (n − 1) at 95% confidence level). As can be

Table 3. Determination of lead, chromium, manganese and zinc in botanic and biological slurry samples

Sample	Analyte	Concentrations of metals (μg g^{-1})				
		Certified value	Without[a]	Recovery (%)	$W + Ir + NH_4H_2PO_4$[a]	Recovery (%)
CRM 155	Pb	104 (71–136)	66 ± 4	63	105 ± 2	101
	Cr	0.59 (0.51–0.66)	0.49 ± 0.04	83	0.57 ± 0.02	97
	Mn	9.30 (8.78–9.82)	7.63 ± 0.51	82	9.23 ± 0.34	99
	Zn	34.3 (32.8–35.7)	25.4 ± 1.5	74	34 ± 1	99
CRM V-10	Pb	1.6 (0.8–1.9)	1.09 ± 0.06	68	1.61 ± 0.03	99
	Cr	6.5 (5.6–7.1)	5.6 ± 0.2	86	6.6 ± 0.1	101
	Mn	47 (32–52)[b]	38.1 ± 1.9	81	45.6 ± 1.4	97
	Zn	24 (21–27)	17.8 ± 1.1	74	23.5 ± 0.6	98
SRM 1575	Pb	10.8 ± 0.5	7.7 ± 0.6	71	10.5 ± 0.3	97
	Cr	2.6 ± 0.2	2.1 ± 0.4	81	2.7 ± 0.1	103
	Mn	675 ± 15	567 ± 26	84	668 ± 12	99
SRM 1570a	Pb	0.2[b]	0.16 ± 0.02	80	0.19 ± 0.01	95
	Mn	75.9 ± 1.9	66.0 ± 2.6	87	74.4 ± 1.6	98
	Zn	82 ± 3	59 ± 4	72	80 ± 2	97
CRM V-9	Pb	0.25 (0.22–0.33)	0.21 ± 0.02	84	0.26 ± 0.01	104
	Cr	0.11 (0.08–0.14)	0.09 ± 0.02	82	0.11 ± 0.01	100
	Mn	0.15 (0.12–0.21)[b]	0.13 ± 0.03	87	0.15 ± 0.01	100
SRM 1577b	Pb	0.129 ± 0.004	0.09 ± 0.01	67	0.13 ± 0.01	101
	Mn	10.5 ± 1.7	8.6 ± 1.8	82	10.2 ± 0.3	97
	Zn	127 ± 16	90 ± 14	71	124 ± 6	98
SRM 1400	Pb	9.07 ± 0.12	5.80 ± 0.41	64	8.80 ± 0.11	97
	Mn	17[b]	14.3 ± 0.9	84	16.7 ± 0.4	98
	Zn	181 ± 3	129 ± 7	71	182 ± 3	101
CRM A-13	Pb	0.18 (0.14–0.30)	0.12 ± 0.01	66	0.18 ± 0.01	102
	Zn	13 (12–14)	9.10 ± 0.5	70	12.6 ± 0.2	97
SRM 1573a	Cr	1.99 ± 0.06	1.61 ± 0.07	81	1.95 ± 0.04	98
	Mn	246 ± 8	212 ± 10	86	248 ± 6	101
	Zn	30.9 ± 0.7	24.1 ± 0.9	78	30.6 ± 0.6	99

[a] Mean of eight replicate measurements of a solution with 95% confidence level, $\overline{X} \pm (ts)/\sqrt{n}$; [b] Not certified.

seen in Table 3, in the absence of a modifier, the percent recovery of analytes is less than 88%. The results obtained with $W + Ir + NH_4H_2PO_4$ are in good agreement with the certified values, and the percent recoveries are in the range of 95–104%. It should be pointed out that the standard deviations of all sample results using $W + Ir + NH_4H_2PO_4$ were lower than those in the absence of a modifier for slurry samples. The 50 µg $NH_4H_2PO_4$ in 0.2% (v/v) Triton X-100 plus 0.2% (v/v) nitric acid mixture is also useful for depressing or reducing interferences in the sample matrix.

Conclusions

The use of $W + Ir + NH_4H_2PO_4$ modifier mixture and its components in 0.2% (v/v) Triton X-100 plus 0.2% (v/v) nitric acid was investigated for the determination of Pb, Cr, Mn and Zn in slurries of botanic and biological standard and certified reference materials by means of ETAAS. Interference effects and analytical problems arising from the sample matrix could be reduced by using the $W + Ir + NH_4H_2PO_4$ modifier mixture and a platform inserted into the graphite tube. Extremely low characteristic masses and detection limits were obtained. The results suggest that the $W + Ir + NH_4H_2PO_4$ modifier mixture proposed is applicable to the determination of Pb, Cr, Mn and Zn in slurries of botanic and biological samples although they have complex matrices.

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