Electrothermal atomic absorption spectrometric determination of cadmium and lead in environmental, botanic and biological samples by different permanent modifiers†

Orhan Acar*

TAEK, Ankara Nükleer Araştırma ve Eğitim Merkezi, 06100 Ankara, Turkey.
E-mail: orhana@taek.gov.tr; Fax: (+90) 312-223-4439; Tel: (+90) 312-212-6230

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Permanent modifiers (Zr, W, Ru, Zr–Ru and Zr–W) thermally deposited on platforms inserted in pyrolytic graphite tubes and Pd + Mg(NO₃)₂ conventional modifier mixture have been employed for the determination of cadmium and lead in dissolved environmental, botanic and biological samples by electrothermal atomic absorption spectrometry (ETAAS). Optimum masses and mass ratios of permanent modifiers for Cd and Pb have been investigated. 240 µg Zr + 240 µg W or 240 µg Zr + 200 µg Ru has been found as efficient as 5 µg Pd + 3 µg Mg(NO₃)₂ for obtaining thermal stabilization and for avoiding most serious interferences. Comparison has been made in terms of pyrolysis and atomization temperatures, atomization and background signal shapes, characteristic masses and detection limits. Long-term stability curves for analytes in samples with Zr, Zr–Ru, Zr–W and Pd + Mg(NO₃)₂ have been obtained. Cadmium and lead contents determined in certified and standard reference materials by using optimum conditions studied were in agreement with the certified reference materials.

Introduction

In recent years, permanent modifiers have been successfully applied to the analysis of real samples in ETAAS leading to several benefits in comparison to conventional modifiers. The main observed advantages such as faster heating programs, better detection limits and longer term signal stability have been described in earlier studies. A procedure for permanent chemical modification consists of the introduction of several aliquots of the chemical modifier solution into the graphite platform, followed by stepwise drying–pyrolysis, thereby obtaining a layer of the modifier thermally deposited on the graphite surface. The Rh, Ru and Ir, as well as carbide forming elements such as Zr and W, have been used as permanent modifiers for the determinations of analytes in various matrices.

The aims of this work are to evaluate the difference in performance of Zr, W, Ru, Zr–Ru and Zr–W and to compare with Pd + Mg(NO₃)₂ for the determination of cadmium and lead in environmental, botanic and biological samples by ETAAS. The evaluation of the Zr–W or Zr–Ru was performed in order to attain at least the same selectivity as Pd + Mg(NO₃)₂ for overcoming interferences in the samples.

Experimental

Instrumentation

All Cd and Pb absorbance measurements were carried out using a 180/80 Model atomic absorption spectrometer (Hitachi, Japan), equipped with a graphite furnace (Hitachi 180/78) with Zeeman-effect background correction, an automatic data processing unit (180/205) and an autosampler. Hollow cathode lamps (Hitachi) for Cd and Pb operated at 7.5 mA (wavelength 228.8 nm and slit 1.3 nm) and 10.0 mA (wavelength 283.3 nm and slit 1.3 nm), respectively, were employed as radiation sources. The instrumental parameters and operating conditions recommended by the manufacturer were used, unless otherwise stated. Argon 99.995% was used as the purge gas, the flow of which was interrupted during atomization. Pyrolytically graphite coated graphite tubes (Hitachi No. 190/6007) inserted with graphite platforms (Hitachi No. 190/6008) and integrated absorbance (peak area) mode were used to obtain absorbance signals throughout. The volume of the sample or calibration solution injected into the platform was 20 µL. The recorder (Varian No 9176) was used in a 20 mV/FS span in order to obtain atomization and background signal profiles. The optimized graphite furnace temperature program is given in Table 1.

Materials, reagents and solutions

Ultrapure water (18.0 MΩ cm) obtained from an Ultrapure water system (Nanopure Infinity, Barstead, Germany) was used throughout to prepare solutions. Analytical grade reagents of HNO₃ (65%, w/w), HCl (37%, w/w), H₂O₂ (35%, w/w), HClO₄ (70–72%, w/w), H₂SO₄ (95–98%, w/w) and HF (40%, w/w) taken from Merck (Darmstadt, Germany) were used. All solutions were stored in high density polypropylene bottles. Plastic bottles, autosampler cups and glassware were washed with a 5% (w/v) HNO₃ solution and rinsed several times with Milli-Q water. Ultrapure water (18.0 MΩ cm) obtained from an Ultrapure water system (Nanopure Infinity, Barstead, Germany) was used throughout to prepare solutions. All solutions were stored in high density polypropylene bottles. Plastic bottles, autosampler cups and glassware were washed with a 5% (w/v) HNO₃ solution and rinsed several times with Milli-Q water.

<table>
<thead>
<tr>
<th>Step</th>
<th>Temperature/°C</th>
<th>Ramp/s</th>
<th>Hold/s</th>
<th>Ar flow rate/ml min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60–130</td>
<td>20</td>
<td>10</td>
<td>250</td>
</tr>
<tr>
<td>2</td>
<td>130–200</td>
<td>20</td>
<td>10</td>
<td>250</td>
</tr>
<tr>
<td>3</td>
<td>200–variable</td>
<td>30</td>
<td>20</td>
<td>250</td>
</tr>
<tr>
<td>4</td>
<td>1350, 1900°</td>
<td>0</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>2200</td>
<td>0</td>
<td>3</td>
<td>250</td>
</tr>
</tbody>
</table>

† Electronic supplementary information (ESI) available: Temperature program for modifier coating; optimization of mass and mass ratio of permanent modifiers and cadmium peak profiles; pyrolysis temperatures; characteristic masses and detection limits of cadmium and lead; and contents and recoveries of cadmium and lead in various reference materials. See http://www.rsc.org/suppdata/ja/b3/b315881k/
materials were cleaned by soaking in 20% v/v HNO₃ for two days and rinsing six times with ultra pure water and dried. The washing water containing 0.2% v/v HNO₃ and 0.2% v/v Triton X-100 was used to clean the sampling capillary and to avoid clogging of the autosampler pipette, thus improving dispensing of the solution on to the platform.

The permanent modifier solutions (1.0 g l⁻¹) of W, Zr and Ru were prepared from 100 mg W powder dissolved in 30% H₂O₂, 353.2 mg ZrOCl₂·8H₂O and 214.1 mg RuCl₃·0.5 H₂O (Merck, Germany) dissolved in 10% HCl solution and diluted to 100 ml with water after evaporation of acids. The 0.05% m/v Pd + 0.03% m/v Mg(NO₃)₂ modifier mixture was prepared from 10.0 g l⁻¹ Pd (Pd(NO₃)₂·2H₂O) and 10.0 g l⁻¹ Mg(NO₃)₂ solutions (Merck).

Analytical calibration standards were prepared from the stock solutions of Cd and Pb (1.0 g l⁻¹) obtained from BDH chemicals (UK) by suitable and serial dilution in 0.2% v/v HNO₃.

Decomposition of samples by microwave-assisted acid digestion

Decomposition of samples was performed in five replicates in Milestone Ethos Sel microwave oven (MLS Ethos 1600, Italy) according to the following procedures described in previous works.1–6

(i) Sediments, soils and coal fly ash. A portion of sample (0.20–0.25 g) was accurately weighed into a Teflon digestion vessel, then 2.0 ml concentrated HNO₃, 1.0 ml concentrated HCl and 1 ml HF were subsequently added to the vessel, with a gentle swirl of the acid mixture. The bomb was closed and placed inside the microwave oven. The steps of the microwave program applied are heating from room temperature to 120 °C for 5 min and waiting at this temperature for 10 min; heating from 120 °C to 180 °C for 10 min and holding for 20 min; and turning off the microwave and waiting for 10 min. After cooling, the bomb cap was withdrawn, and the open vessel was placed on a hot plate. Sample was boiled nearly to 2 ml in order to evaporate the excess acid. Excess of HF was eliminated using 1 ml concentrated H₂SO₄.

If a residue of material remained, the decomposition procedure was repeated until it was dissolved completely. The final solution was transferred to a 25–100 ml volumetric flask by washing the interior surface of digestion vessel with 2% (v/v) HNO₃ three times and the final acidity of flask was adjusted to 1% (v/v) HNO₃.

(ii) Biological and botanical materials. A portion of sample (0.20–2.00 g) was accurately weighed into a Teflon digestion vessel, 4.0 ml concentrated HNO₃ and 2.0 ml H₂O₂ were subsequently added to the vessel. Decomposition was carried out using the heating program and procedure mentioned above. The final temperature was set to 160 °C. After adding 3 ml HNO₃, 1 ml HCl and 1 ml HF into the two Teflon bombs, and 3 ml HNO₃ and 2 ml H₂O₂ to other two bombs, they were heated up to 130 °C for 20 min by using a microwave heating program in order to prepare decomposition. The bomb was closed and placed inside microwave oven. The steps of the microwave program applied were swirl of the acid mixture. The bomb was closed and placed inside the microwave oven. The steps of the microwave program applied were heating from room temperature to 120 °C for 5 min and waiting at this temperature for 10 min; heating from 120 °C to 180 °C for 10 min and holding for 20 min; and turning off the microwave and waiting for 10 min. After cooling, the bomb cap was withdrawn, and the open vessel was placed on a hot plate. Sample was boiled nearly to 2 ml in order to evaporate the excess acid. Excess of HF was eliminated using 1 ml concentrated H₂SO₄.

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Results and discussion

Optimization of ETAAS conditions

Cadmium and lead are routinely determined volatile elements in various samples.1,6,7 They are lost at temperatures higher than 200 °C for Cd and 500 °C for Pb in the absence of a chemical modifier.4 In order to minimize organic or inorganic matrix effects, use of the conventional or permanent modifiers, which provide pyrolysis temperatures at least 500 °C for Cd and 700 °C for Pb, are required for accurate determinations of cadmium and lead in real samples.1,4,6,7,9,11,15

Coatings of Zr, W and Ru on the platforms were thermally performed, in similar ways described in previous works.2,7,9,10,14 by injecting 40 µl of each 1.0 mg l⁻¹ modifier solution, respectively, onto the platform and submitting the tube to the temperature program given in Electronic supplementary information (ESI)† (Table S1). In order to prepare Zr–W or Zr–Ru coated platforms, the platforms were firstly treated with Zr and then further treated with W or Ru solution, followed by step wise drying and pyrolysis. The 20 µl of 2.5 µg l⁻¹ Cd and 50.0 µg l⁻¹ Pb aqueous solutions, coal fly ash (Cd content 2.05 ± 0.02 µg l⁻¹) and estuarine sediment (Pb content 40.0 ± 4.1 µg l⁻¹) were delivered into the platforms coated with different mass of permanent modifiers.

Absorbance values of analytes versus mass and mass ratio of permanent modifiers coated on the platforms are given in ESI† (Fig. S1). Higher analytical signals (sensitivities) for Cd and Pb in aqueous and sample solutions were obtained when 240 µg W, 200 µg Ru, 240 µg Zr + 200 µg Ru and 240 µg Zr + 240 µg W were deposited onto the platform. When higher modifier mass was deposited, analytical signals decreased, double and broader peaks were observed.5,8 When cleaning temperature was exceeded 2200 °C (Table 1), the coating lifetime was decreased. Therefore, final temperatures of heating programs and coating procedures were increased up to 2200 °C and 2000 °C, respectively, in order to avoid the removal of modifier coating from the platform (Table 1 and ESI Table S1†). The 60 °C in both tables was necessary to prevent material from spilling out of the tube.

Pyrolysis and atomization temperatures for Cd and Pb in sample solutions obtained by permanent modifiers and Pd + Mg(NO₃)₂ modifier mixture (added at each firing) are given in Tables 1 and S2. As can be seen, although the pyrolysis temperatures of cadmium and lead in biological and botanical samples are the same or lower by –50 °C than in soils and sediments, they are higher than 500 °C for Cd and 700 °C for Pb. Generally, it is desirable to use pyrolysis temperatures given in Table S2† as high as possible in order to remove the matrix effects and background signals efficiently without losing analyte mass. The maximum pyrolysis temperatures obtained with Zr–Ru or Zr–W were higher than those obtained with Zr, Ru and W. The temperatures found were compared with the previous studies1–6,7,9–11,14 and similar results were observed. The small differences were ascribed to the particular instrument and different batch of platforms used. The mixture of 5 µg Pd + 3 µg Mg(NO₃)₂ was the most suitable to obtain reproducible signals as well as good cadmium and lead recoveries among the various chemical modifiers described in previous works.11,15

Atomization profiles of analytes

Atomization and background profiles of Cd and Pb by injecting 20.0 µl of sample solutions onto the platforms coated with permanent modifiers were obtained and they are shown in ESI† (Fig. S2) for Cd as an example. As can be seen, signal/noise ratios of Cd with Zr–Ru or Zr–W were higher when compared with Zr. For comparison with Zr, when Zr–W or Zr–Ru modifier mixture was used, sharp and narrow peaks were obtained and small shift to a later in maximum times (t_max) of absorbance profiles were observed. There were no significant differences at the appearance times (t_app) of the peaks. Therefore, Zr–Ru or Zr–W can be used for the determination of Cd and Pb in samples.

Analytical characteristics

Calibrations were carried out against aqueous standard solutions with linear ranges extending up to 5 µg l⁻¹ for Cd and 80 µg l⁻¹ for Pb. Characteristic masses (mₜ) and limits of detection (LOD, 3σ criterion) obtained for the analytes employing different permanent modifiers and Pd + Mg(NO₃)₂ based on the integrated absorbance were calculated from the 20 consecutive measurements of the blank solutions (1.0% v/v HNO₃) according to IUPAC21 and previous studies.3–5 The mₜ and LOD obtained are given in Table S3†. All correlation coefficients (r) found were higher than 0.99. As can be seen, better characteristic masses and
the lowest detection limits were obtained with mixed Zr-Ru and Zr-W modifiers in relation to single modifiers. Better detection limits could be attained, since the volatile impurities of the modifier solution are eliminated during the thermal pretreatment of the atomizer. High detection limits obtained with the conventional modifier may be attributed to high blanks in the palladium solution.

### Stabilization studies of coated platforms

Coating of platforms with modifiers increases tube lifetime by 50–110% when compared with untreated pyrolytic carbon platforms. Cadmium and lead long-term stability curves obtained by Zr, Zr-W or Zr-Ru coated platforms and pyrolytic carbon platform with 5 µg Pd + 3 µg Mg(NO₃)₂ modifier mixture in dissolved Buffalo river sediment (2704) and Hay powder (V-9) are presented in Fig. 1A and B, respectively. With the Zr-W or Zr-Ru permanent modifier (n = 1200–1300 firings), the tube lifetime obtained was 95–110% higher than the untreated platforms with use of Pd + Mg(NO₃)₂ (n = 550–600 firings), when reconditioning platform treatments were performed during nine working days with 8 h of instrument operation for each analyze. It is important to point out that each platform treatment lasted for about 300–350 analytical firings when working with dissolved biological and environmental samples (Fig. 1A and B). The treated platform used could be reconditioned by performing five firings at 2700 °C for 5 s for clean-out, and subsequently carrying out the treatment procedure as described before. The new recoated platform again lasted for 300–350 firings with sensitivity not significantly different (<3%) from the first coating. The total time for treatment of the graphite surface with Zr-W or Zr-Ru is about 40 min.

The repeatability of analytical signals obtained with the Zr-W or Zr-Ru coatings is superior to the Pd + Mg(NO₃)₂ throughout the atomizer lifetime. Variations of sensitivity during the analytical firings are lower for the permanent modifier (RSD 5.3%, n = 350) as compared with the chosen conventional modifier (RSD 15.4%, n = 650). As can be seen, at least 30% longer tube lifetimes were obtained with Zr-Ru and Zr-W when compared with single permanent modifiers.

### Analysis of samples

The accuracy and the performance of the proposed method employing 240 µg Zr, 240 µg W, 200 µg Ru, 240 µg Zr + 200 µg Ru and 240 µg Zr + 240 µg W and 5 µg Pd + 3 µg Mg(NO₃)₂ were assessed with dissolved samples for the determination of cadmium and lead. The contents and analyte recoveries obtained are given in Table S4. The results were presented as an average ± confidence interval (n = 5 replicates of sample where each one was measured five times). As can be seen, recoveries of Cd and Pb obtained by using Zr-W or Zr-Ru (97–104%) are higher than that obtained with the single permanent modifiers (<90%). It should be pointed out that the standard deviations of the results obtained using Zr-Ru or Zr-W are lower than the Pd + Mg(NO₃)₂.

As a result, better analytical characteristics were obtained with Zr-W and Zr-Ru when compared with single permanent and Pd + Mg(NO₃)₂ conventional modifiers. The proposed Zr-W or Zr-Ru permanent modifier mixture can be applied to the direct determination of trace amounts of Cd and Pb in environmental, botanic and biological samples containing complex matrices without chemical treatment.

### Acknowledgements

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### References


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**Fig. 1** Long-term stability curves for untreated and Zr-W, Zr-Ru or Zr treated platforms. Each point represents an average of ten measurements after injection of 20 µl of dissolved: (A) Buffalo river sediment, SRM 2704 (Cd content 50.4 ± 3.2 µg per injection); (B) Hay powder, CRM V-10 (Pb content 872 (437–1038) pg per injection). Arrows indicate a new coating of platform with Zr and Zr followed by W or Ru. ---, 240 µg Zr; —, 240 µg Zr + 240 µg W; —, 240 µg Zr + 200 µg Ru permanent modifiers.