

# Application of high-energy polarised beam energy dispersive X-ray fluorescence spectrometry to cadmium determination in saline solutions

Katleen Van Meel,<sup>a</sup> Clàudia Fontàs,<sup>b</sup> René Van Grieken,<sup>a</sup> Ignasi Queralt,<sup>c</sup> Manuela Hidalgo<sup>b</sup> and Eva Marguí<sup>\*b</sup>

Received 30th November 2007, Accepted 27th March 2008

First published as an Advance Article on the web 21st April 2008

DOI: 10.1039/b718382h

In the present work, the analytical performance of a methodology based on a preconcentration using activated thin layers followed by high-energy polarised beam energy-dispersive XRF spectrometry (HE-P-EDXRF) for the determination of trace amounts of Cd in saline solutions is presented. Linear calibration curves were obtained over the range 5–8000  $\mu\text{g L}^{-1}$  of Cd. When comparing the developed method to the direct analysis of Cd in sea water, the detection limits were improved by several orders of magnitude, with values of 2.25  $\mu\text{g L}^{-1}$  ( $\text{Al}_2\text{O}_3$  target) and 0.075  $\mu\text{g L}^{-1}$  (CsI target), respectively. The accuracy was checked by analyzing spiked natural sea water at Cd concentrations of 20, 100 and 600  $\mu\text{g L}^{-1}$  and results were compared to those obtained with anodic stripping voltametry and no significant differences at the 95% confidence level were found. The method has a good reproducibility over the investigated period of time and the precision of the method was better than 10%.

## 1. Introduction

The monitoring of heavy metals such as Cd in coastal and open sea water is becoming increasingly important.<sup>1</sup> Normally, Cd concentrations in sea water are in the  $\text{ng L}^{-1}$  range, and the analytical procedures used for its determination are usually based on anodic stripping voltametry (ASV)<sup>2</sup> and atomic spectrometry.<sup>3,4</sup>

X-ray fluorescence spectrometry (XRF) has been a popular method for major elemental analysis in geological samples to avoid complicated acid-digestion procedures. In particular, the speed, accuracy, and versatility of XRF are the most important features among the many that have made it a very mature analytical tool for routine quality control in many industries, as well as analytical support for the research laboratory.<sup>5</sup> However, direct XRF analysis of solutions entails technical difficulties and is characterized by essential errors of the results. Moreover, liquid samples usually provide a high X-ray scatter background resulting in poor signal-to-noise ratio. Typical detection limits of conventional direct XRF with 30 min counting time are in the  $\text{mg L}^{-1}$  range<sup>6</sup> which is not satisfactory for environmental requirements. The sensitivity can be improved using total reflection X-ray fluorescence spectrometry (TXRF). As a consequence of the configuration of the TXRF systems, the high background that would generally occur due to scatter from the sample support is absent and, therefore, concentrations in the range of several  $\mu\text{g L}^{-1}$  can be measured in aqueous samples such as drinking water,<sup>7</sup> rain water<sup>8</sup> and stream waters<sup>9,10</sup> without preconcentration.<sup>11</sup> However, when dealing with the analysis of waste and sea water, also a special preparation method has to be

applied to separate the suspended matter and to remove the salt content prior to the measurement.<sup>1</sup>

Many different chemical and physical preconcentration techniques have been proposed.<sup>12–14</sup> Nevertheless, these preconcentration methods usually involve the addition of reagents, adjusting the pH of test samples, laborious filtrations and drying stages, with the possibility of contamination of samples during the sample preparation.

Another fact that has limited the use of conventional XRF spectrometry for the analysis of some important pollutant elements such as Cd has been the insufficient sensitivity of the technique inherent to the use of L-series spectral lines measured to quantify high atomic number elements.<sup>15</sup>

In the present work, the analytical performance of a methodology based on a preconcentration using activated thin layers with the commercial anion-exchanger Aliquat 336 followed by high-energy polarised beam energy-dispersive XRF spectrometry (HE-P-EDXRF) for the determination of trace amounts of Cd in saline solutions is presented. Analytical figures of merit such as linearity, limits of detection, accuracy, repeatability and reproducibility over the time have been evaluated. Furthermore, a study has been carried out to evaluate the analytical improvements of the proposed methodology for Cd determination with respect to the direct analysis of sea water.

## 2. Experimental

### 2.1. Preconcentration of cadmium

The methodology used to determine Cd in saline solutions is based on the principles of metal preconcentration using activated thin layers containing the commercial extractant tricapryl-methylammonium chloride (Aliquat 336). Based on the results of a previous work,<sup>16</sup> a polyvinylidene difluoride film (Durapore, Millipore; average pore-size of 0.2  $\mu\text{m}$ , porosity of 75%, and average thickness of 125  $\mu\text{m}$ ) was used to contain the extractant solution. To activate the thin layer, the polymeric support was

<sup>a</sup>Department of Chemistry, Environmental Analysis Group, University of Antwerp, Universiteitsplein, 1, Antwerp, B-2610, Belgium

<sup>b</sup>Department of Chemistry, University of Girona, Campus Montilivi, Girona, E-17071, Spain

<sup>c</sup>Laboratory of X-Ray Analytical Applications, Institute of Earth Sciences "Jaume Almera", CSIC, Solé Sabarís s/n, Barcelona, E-08028, Spain

soaked in a 500 mM solution of Aliquat 336 in decaline for 10 min and then taken out of the organic solution and wiped with a piece of filter paper.

The collection of Cd on the thin layers for both standards and samples was carried out by using a cell, where the activated films were placed in a circular window, 3.8 cm diameter, and facing the source solution consisting of 190 mL of Cd solution in 2 M HCl stirred at 800 rpm for 150 min. At the end of the experiments, activated thin layers containing the extracted Cd were retired from the cell, washed with deionized water several times and let to dry at room temperature before XRF analysis.

## 2.2. Instrumental and operating conditions

For the XRF analysis of activated thin layers and sea water samples, the Epsilon-5 instrument (PANalytical, Almelo, The Netherlands) was used. Epsilon-5 is a high-energy EDXRF spectrometer, using a polarizing beam, equipped with a 600 W Gd-anode and a high purity Ge-detector. There are 13 secondary targets (Al, CaF<sub>2</sub>, Ti, Fe, Co, Ge, KBr, Zr, Mo, Ag, CsI, CeO<sub>2</sub> and W) and two Barkla-scatterers (Al<sub>2</sub>O<sub>3</sub> and B<sub>4</sub>C) available. Detailed information about features of the Epsilon-5 instrument can be found elsewhere.<sup>15</sup>

The metal loaded thin layers were measured directly in circular stainless-steel cups of 50 mm diameter with a circular hole in the bottom facing the detector and the secondary target, thus enabling the analysis of an area of 34 mm diameter. For the direct analysis of liquid samples, aliquots of 7 mL were deposited in special liquid sample holders which incorporate tapered snap-on ring at the end of the cell for attachments of thin-film liquid sample support.

Spectrum evaluation and fitting was performed using the built-in software of the equipment based on the QXAS-AXIL code.<sup>17</sup>

Operating conditions used were displayed in a previous work.<sup>16</sup>

The voltammetric equipment used as a reference technique for the analysis of the spiked sea water samples consisted of a Stand (Metrohm, Switzerland) polarograph equipped with a hanging mercury drop electrode, a Ag/AgCl reference electrode and a Pt counter electrode. Measurements were made in acetate buffer by the standard addition method using the recommended operating conditions by the manufacturer.

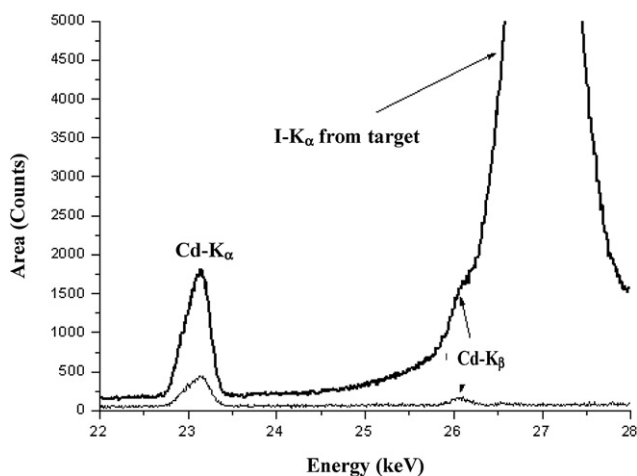
## 3. Results and discussion

### 3.1. Secondary target evaluation for Cd analysis by HE-P-EDXRF

Taking into account the suitable excitation energies to increase the X-ray production for the Cd-K lines, two targets were tested: Al<sub>2</sub>O<sub>3</sub> (Barkla target) and CsI (secondary target).

Since the Al<sub>2</sub>O<sub>3</sub> is only capable of scattering the original beam from the Gd-anode, no characteristic peaks, except for Gd, are emitted when using this target. In contrast, the CsI secondary target emits its characteristic energies (Cs-K $\alpha$  and I-K $\alpha$ ) that are very close to the K-absorption edge of Cd, resulting in very intense Cd-peaks and a good sensitivity.

For some applications, additional metal foils can be used as filters between the secondary target and the sample to reduce the background continuum. Nevertheless, in this case, no primary



**Fig. 1** Spectra for a standard solution containing 100  $\mu\text{g L}^{-1}$  of Cd using Al<sub>2</sub>O<sub>3</sub> target (grey spectrum) and CsI target (black spectrum).

beam filter was applied, since a previous study<sup>16</sup> revealed that for the analysis of Cd in activated thin layers, the best signal-to-noise ratio was achieved when no primary beam filter was used.

In Fig. 1, spectra for a standard solution of 100  $\mu\text{g L}^{-1}$  of Cd using both targets are displayed. Data attained as cps mA<sup>-1</sup> confirmed that the sensitivity for Al<sub>2</sub>O<sub>3</sub> target is approximately 4 times smaller than CsI target. However, when using CsI target, the Cd-K $\beta$  peak is overlapped with the I-K $\alpha$  peak from the target, which might hamper the fitting. In the present research, only Cd-K $\alpha$  is used for quantification purposes and the theoretical ratio between  $\alpha$  and  $\beta$  peaks, which is often used to help the fitting, is ignored so that the peaks are fitted separately. It can therefore be stated that the expected problems with the spectral overlap in the case of the CsI target do not influence the fitting of Cd peak.

### 3.2. Analytical figures of merit for the HE-P-EDXRF method after thin layer preconcentration

In order to check the real effectiveness of both targets for Cd analysis after thin-layer preconcentration, analytical figures of merit as linearity, limit of detection, accuracy, repeatability and reproducibility were evaluated.

For the linearity study, various aqueous samples containing Cd concentration in 2 M HCl in the range of 5–8000  $\mu\text{g L}^{-1}$  were taken throughout the whole preconcentration and detection procedure described above. Two different concentration regions were chosen: a high concentration range (100–8000  $\mu\text{g L}^{-1}$ ) and a low concentration range (5–100  $\mu\text{g L}^{-1}$ ). The calibration curves for both targets in both concentration regions are shown in Fig. 2. A good linearity and a wide working range under experimental conditions were obtained without the need of matrix and thickness effect corrections, commonly required in XRF analysis.

Detection limits (in  $\mu\text{g L}^{-1}$ ) were calculated as three times the standard deviation of Cd signal in a blank sample divided by the sensitivity. Results show that the LoD achieved using CsI as secondary target (0.075  $\mu\text{g L}^{-1}$ ) for the determination of Cd in sea water samples was almost 30 times lower than those obtained

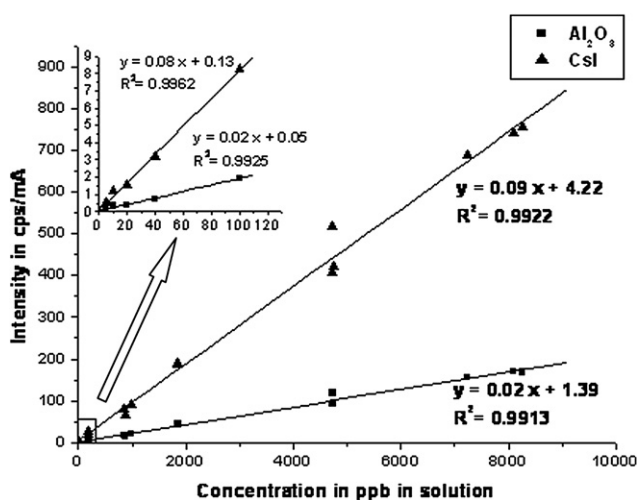


Fig. 2 Calibration curves for Cd using Al<sub>2</sub>O<sub>3</sub> and CsI targets.

using the Barkla scatterer (2.25 μg L<sup>-1</sup>). Moreover, the LoDs achieved in this work are comparable, and, in most cases lower, than those reported in literature for the determination of Cd in different aqueous matrices using XRF spectrometry (see Table 1).

The accuracy was checked by applying the proposed methodology for the analysis of duplicate natural sea water spiked at 20, 100 and 600 μg L<sup>-1</sup>Cd. As Table 2 shows, Cd added to the samples was quantitatively determined using both studied targets.

Moreover, the Cd concentrations determined by the proposed analytical method and by the AVS technique were in very good agreement and no significant differences at the 95% confidence level were found. Thus, the accuracy of the procedure and the absence of matrix effects were confirmed for this type of high salinity samples.

In order to study the global precision of the proposed method, 4 independent solutions containing 45 μg L<sup>-1</sup> of Cd were pre-concentrated and measured under the same experimental conditions using both targets. Relative standard deviations from the obtained results were calculated, being 6.5% for Al<sub>2</sub>O<sub>3</sub> and 4.7% for CsI targets. Besides, one of the activated thin layers was

Table 2 Comparison of Cd concentrations obtained on spiked sea water samples by HE-P-EDXRF and ASV<sup>a</sup>

Cadmium added/μg L <sup>-1</sup>	HE-P-EDXRF		
	Al <sub>2</sub> O <sub>3</sub> target	CsI target	ASV
20	20 (s = 2)	21 (s = 3)	26 (s = 3)
100	102 (s = 3)	100 (s = 5)	106 (s = 4)
600	553 (s = 79)	582 (s = 76)	617 (s = 6)

<sup>a</sup> s: standard deviation.

measured four times and the relative standard deviation associated was also calculated. This repeatability is related to the instrument and counting statistics and it was found that it was better than 2.5% for both targets. The reproducibility over the time for the method was examined by analyzing 5 replicate preparations of a 45 μg L<sup>-1</sup> Cd solution during 6 days, spread over two weeks. The results were statistically analyzed using ANOVA. Judging from these results, it can be said that the method has a good reproducibility over the investigated period of time and the expected precision of the method is for both targets better than 10%. On the other hand, the very limited differences in the fluorescent intensities after several irradiations demonstrated the absence of damage of the activated thin layer.

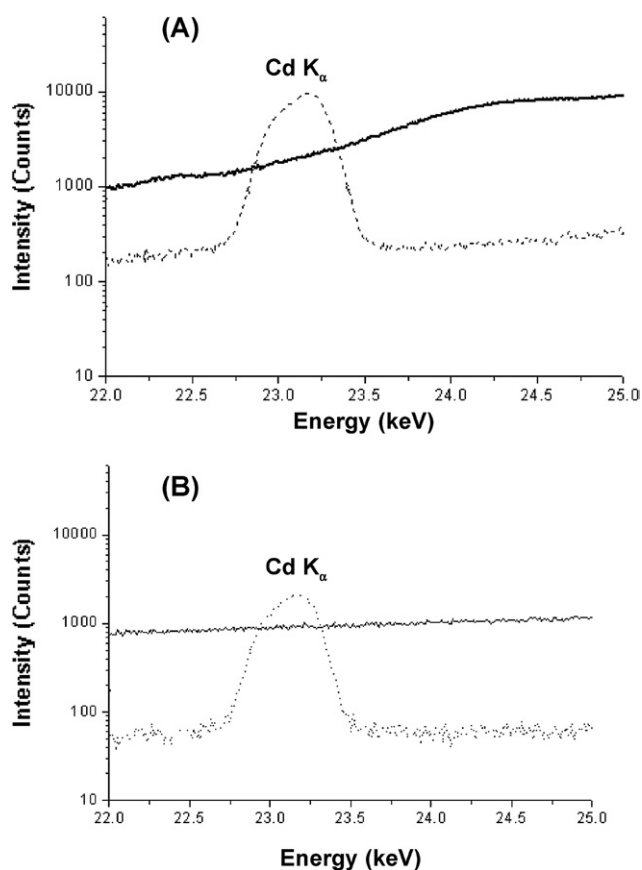
### 3.3. Comparison of direct analysis of sea water samples with the proposed method

A study was conducted to compare the analytical improvements of the proposed methodology for Cd determination with the direct analysis of saline solutions. For this purpose, an aliquot of 7 mL of a spiked sea water sample at the level of 5000 μg L<sup>-1</sup> of Cd was analyzed directly with the HE-P-EDXRF spectrometer. A small peak of Cd could be distinguished in the obtained spectrum. If the parameters for this spectrum are used to estimate the detection limit according to the 3σ approach, a detection limit of approximately 600 μg L<sup>-1</sup> can be expected. Considering the LoDs for Cd obtained in the case of preconcentration using activated thin layers (Al<sub>2</sub>O<sub>3</sub>: 2.25 μg L<sup>-1</sup>, CsI: 0.075 μg L<sup>-1</sup>) it is clear that the proposed method offers huge benefits. In Fig. 3, the spectra obtained for the direct analysis of a sea water sample

Table 1 Comparison of published methods based on XRF spectrometry for the determination of Cd in water samples<sup>a</sup>

Instrumentation	Preconcentration procedure	Sample	Time/s	LoD/μg L <sup>-1</sup>	Ref.
TXRF (W tube, 59 kV, 33 mA)	Without preconcentration			0.260	
	Freeze-dried	Rain water	1000	0.040 <sup>b</sup>	8
	Reverse-phase technique			0.020	
TXRF (W tube, 50 kV, 38 mA)	Without preconcentration	Drinking water	200	4.9	7
WDXRF (60 kV, 50 mA, LiF200)	Without preconcentration	Mine waste water	NA	300	18
WDXRF (Ag tube, 12–50 kV, 20–50 mA, LiF002)	Extractive enrichment and re-extraction in aqueous phase to obtain gel-like specimens	Waste water	NA	10	19
WDXRF (Rh tube, 50 kV, 80 mA, LiF200)	Iminodiacetate extraction disk (IED)	Environmental water	20	7.1	20
WDXRF (NA)	Chelating solid-phase extraction disks	Drinking water	NA	3.8	21
HE-P-EDXRF (Gd tube, 100 kV, 6 mA)	Activated thin layers (Extractant: Aliquat 336)	Sea water	1000	2.25 (Al <sub>2</sub> O <sub>3</sub> target) 0.075 (CsI target)	This work

<sup>a</sup> NA: Not available. <sup>b</sup> Theoretical LoD derived from the peak-to-background radiation in the XRF spectra instead of defined by the standard deviations of the blank values (3σ<sub>blank</sub>).



**Fig. 3** Comparison between spectra obtained for the direct analysis of a sea water sample containing  $600 \mu\text{g L}^{-1}$  of Cd (straight lines) and after the developed preconcentration step (broken lines) for CsI target (A) and  $\text{Al}_2\text{O}_3$  target (B).

containing  $600 \mu\text{g L}^{-1}$  of Cd and after applying the developed preconcentration step for CsI target (A) and  $\text{Al}_2\text{O}_3$  target (B) are displayed. As can be seen, a very intense peak is found in the case of the activated thin layer preconcentration while in the case of the direct analysis of the liquid samples the signal is obviously below the detection limit. From the same figure, the reduction of the background spectrum could be appreciated when using the preconcentration procedure proposed.

#### 4. Conclusions

In this work, the feasibility of using high-energy polarised beam energy-dispersive X-ray fluorescence spectrometry after activated thin layers preconcentration for Cd determination in saline solutions has been confirmed.

The fact that the background is drastically reduced when using activated thin layers makes possible an improvement of the sensitivity by several orders of magnitude compared to the method of direct analysis of seawater, offering benefits concerning both better detection limits and selectivity.

On the other hand, the use of secondary targets, polarizing geometry and a high energy X-ray tube in the HE-P-EDXRF spectrometer as detection system allows performing the XRF

analysis using K-lines of Cd leading to the improvement of sensitivity and, thus, overcoming the difficulties in the determination of high atomic number elements when employing conventional XRF instrumentation. From data obtained it can be deduced that the sensitivity for  $\text{Al}_2\text{O}_3$  target is approximately a factor of 4 lower than that obtained for the CsI target. However, both targets present similar analytical performance (linearity, accuracy, repeatability, reproducibility over the time, selectivity) when working at the Cd levels studied. The limits of detection for cadmium achieved in the present work ( $\text{Al}_2\text{O}_3$ :  $2.25 \mu\text{g L}^{-1}$  and CsI:  $0.075 \mu\text{g L}^{-1}$ ) are comparable, and in most cases much better, than those obtained in other published works for the determination of Cd in different aqueous matrices using XRF spectrometry and are also competitive with those determined using other popular spectrometric techniques such as FAAS and ICP-AES.

#### 5. Acknowledgments

This research has been developed in the framework of the Spanish National Research Programme (Projects: CGL2004-05963-C04/HID and CGL2007-66861-C4).

#### References

- 1 A. C. M. Costa, M. J. Anjos, R. T. Lopes, C. A. Pérez and C. R. F. Castro, *X-Ray Spectrom.*, 2005, **34**, 183–188.
- 2 F. W. Fifield and P. J. Haines, *Environmental Analytical Chemistry*, Balchic Academia & Professional, London, 1997.
- 3 D. Colbert, K. S. Johnson and K. H. Coale, *Anal. Chim. Acta*, 1998, **377**, 255–262.
- 4 H.-W. Liu, S.-J. Jiang and S.-H. Liu, *Spectrochim. Acta, Part B*, 1999, **54**, 1367–1375.
- 5 T. D. Hettipathirana, *X-Ray Spectrom.*, 2001, **30**, 330–337.
- 6 J. Injuk and R. Van Grieken, *Handbook of X-Ray Spectrometry*, ed. R. Van Grieken and A. A. Markowicz, Marcel Dekker Inc., New York, 1993, pp. 657–692.
- 7 M. A. Barreiros, M. L. Carvalho, M. M. Costa, M. I. Marques and M. T. Ramos, *X-Ray Spectrom.*, 1997, **26**, 165–168.
- 8 R.-P. Stössel and A. Prange, *Anal. Chem.*, 1985, **57**, 2880–2885.
- 9 A. F. Marques, I. Queralt, M. L. Carvalho and M. Bordalo, *Spectrochim. Acta, Part B*, 2003, **58**, 2191–2198.
- 10 M. M. Costa, M. L. Carvalho, M. A. Barreiros and I. Queralt, *X-Ray Spectrom.*, 1999, **28**, 410–413.
- 11 P. Wobrauschek, *X-Ray Spectrom.*, 2007, **36**, 289–300.
- 12 R. Van Grieken, *Anal. Chim. Acta*, 1982, **143**, 3–34.
- 13 R. Jenkins, *X-Ray Fluorescence Spectrometry*, ed. J. D. Winefordner, John Wiley & Sons, Inc., New York, 1999, pp. 149–150.
- 14 A. Montero Álvarez, J. R. Estévez and R. Padilla Álvarez, *J. Radioanal. Nucl. Chem.*, 2000, **245**, 485–489.
- 15 *Epsilon 5 User's Manual*, PANalytical, Almelo, The Netherlands, 2nd edn, March, 2003.
- 16 E. Marguí, C. Fontàs, K. Van Meel, R. Van Grieken, I. Queralt and M. Hidalgo, *Anal. Chem.*, 2008, **80**, 2357–2364.
- 17 *QXAS/AXIL User's Manual*, International Atomic Energy Agency, Vienna, 1992.
- 18 B. Kot, R. Barnowski and A. Rybak, *Pol. J. Environ. Stud.*, 2000, **9**, 429–431.
- 19 L. P. Eksperiandova, A. B. Blank and Y. N. Makarovskaya, *X-Ray Spectrom.*, 2002, **31**, 259–263.
- 20 W. Abe, S. Isaka, Y. Koike, K. Nakano, K. Fujita and T. Nakamura, *X-Ray Spectrom.*, 2006, **35**, 184–189.
- 21 X. Hou, H. L. Peters, Z. Yang, K. A. Wagner, J. D. Batchelor, M. M. Daniel and B. T. Jones, *Appl. Spectrosc.*, 2003, **57**, 338–342.