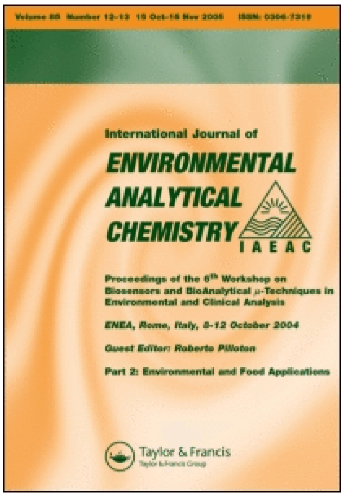

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Recent Methodological Progress in Cadmium Analysis

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Recent Methodological Progress in Cadmium Analysis

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The state-of-the-art of methodology for cadmium analysis in biological and environmental materials on the basis of recent progress is discussed. There is a remarkable gain in sensitivity and reliability for atomic spectroscopy mainly for graphite furnace techniques but to some extent also for flame atomic absorption with Zeeman background correction. Further, the introduction of new commercial polarographic analyzers offering square wave voltammetry made this method less prone to sample pretreatment performance, particularly for the analysis of somewhat higher contents. Another promising new and sensitive method is Total Reflection X-ray Fluorescence (TXRF). From this technical progress together with more or less "classical" methods as isotope dilution mass spectrometry, instrumental, radiochemical and the recently introduced *in vivo*-neutron activation analysis, together with the increased availability and use of biological and environmental reference materials a broad selection of appropriate analytical approaches is at hand now for numerous research and surveillance duties.

KEY WORDS: Cadmium analysis, atomic spectroscopy, voltammetry, total reflection XRF, mass spectrometry, neutron activation analysis, reference materials, matrix effects, quality control.

INTRODUCTION

Cadmium is of particular importance in human and ecotoxicology due to widespread man-made emissions in the atmosphere that have produced a significant global as well as regional pollution and

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occupational exposure which may cause adverse health effects.[1,2] For this reason there have been efforts for years to develop more effective, fast, precise and accurate methods of analysis for this element in numerous materials by a number of classical and modern analytical methods.[3–6] This has led to instrumental and methodological concepts that enabled the quite reliable determination of cadmium down to levels that could not be analyzed successfully before and thus to comparatively accurate estimations of cadmium concentrations in basic food (total diets), body fluids, sea, river and lake water and deposition (rain and snow).[1,2,4]

Nevertheless, due to contamination, pretreatment and matrix problems, still uncertainties existed for extremely low levels in difficult materials as could be shown, e.g., by various interlaboratory comparisons for cadmium in whole blood and urine, mainly performed within the International Union of Pure and Applied Chemistry (IUPAC)[4,7–9]

In very recent years, however, a remarkable methodological progress took place, especially where pretreatment and matrix interferences are concerned. This was particularly the case for some modes of atomic spectroscopy, voltammetry and X-ray fluorescence. But also other, more classical methods like mass spectrometry and neutron activation as well as the increased production and certification of appropriate Reference Materials contributed significantly.[10,11] After summarizing recent findings for probable average levels of cadmium in a selection of biological and environmental materials this paper presents a critical overview on the present potential of the above mentioned analytical methods and means already taken or soon available to improve analytical performance.

CADMIUM LEVELS IN SOME TYPICAL BIOLOGICAL AND ENVIRONMENTAL MATERIALS

Table I shows typical cadmium levels in biological and environmental materials that have been published recently. Values are listed only when they have been confirmed independently or when they were obtained by laboratories which applied rigid and well documented internal and external quality control (QC) programmes. Thus these data are believed to approach as closely as possible today's state-of-the-art "true" average levels or ranges in the materials listed.

TABLE I

Typical cadmium levels in a selection of human and other materials from recent investigations

Material	Probable average content (μg/l or μg/kg)	Approx. range of contents (μg/l or μg/kg)	Remarks
Total diets	<30	15–40	
Human brain	—	6–25	preliminary data
Crude oil and oil products	<1	$\leqq 0.001$–1.0	
Whole blood, nonexposed nonsmokers	$\leqq 0.5$	<0.1–2.0	
Urine, nonexposed nonsmokers	<0.5	$\leqq 0.05$–2.0	
Rain water, rural regions	<0.2	<0.02–1.0	
Retail and human milk various regions	$\leqq 0.05$	<0.02–0.5	
Open sea water, surface	<0.005	0.0001–0.05	
Arctic snow, lowest levels	<0.0002	—	preliminary data

ANALYTICAL METHODS

From recent instrumental improvements a significant gain in detection power and reliability for the analysis of cadmium and other metals is evident.[6,10] In Table II the virtues of the methods discussed below in some detail are compared. As far as *atomic spectroscopy* is concerned, remarkable progress could be achieved for graphite furnace atomic absorption spectroscopy (GFAAS).[10,12–14]

Highly resistant graphite tubes, graphite tubes coated with pyrocarbon and more flexible furnace systems together with dedicated computers offered numerous technical improvements. These included fast and variable temperature ramping steps, alternate sheath gases permitting, e.g., with oxygen as charring aid, in-tube decomposition of complex matrices without any sample pretreatment,[15–18] and platform techniques (L'vov platforms) leading to a significant extension of applications. Matrix and/or element modification together with the very effective Zeeman and Smith–Hieftje background correction systems finally completed the instrumental potential. Thus the intro-

TABLE II

Detection limits of the most important methods for cadmium; the detection limit is defined as three times the Standard Deviation (S.D.) of noise or blank in non interfering analyte solution (NAA: non interfering matrix). Values given in μg/l (μg/kg for NAA).

Method	Detection limit
Voltammetry (film electrode)	<0.0002
AAS, graphite furnace[a]	$\leqq 0.003$
Total reflection XRF[a]	0.4
Neutron activation analysis[b]	$\leqq 1.5$
Inductively coupled plasma-atomic emission spectroscopy (ICP-AES)	<3
AAS with flame (Zeeman background correction)	3

[a] Usually a 50 μl sample volume is considered; if higher sample volumes can be taken, the D.L. is lower.

[b] Sophisticated radiochemical separation procedures (see e.g. reference 31) attain detection limits well below 1 μg/kg.

duction of the so-called stabilized temperature platform furnace (STPF) concept as a combination of all these components frequently allowed peak area evaluation instead of previously applied peak height evaluation. As far as accuracy is concerned this was a promising step towards more reliable GFAAS data and possibly also towards absolute analysis since using the STPF concept, irrespective of the matrix, very similar peak area values could be obtained for the same cadmium amounts in different materials as a proof that calibration by aqueous standards now is within realization.[14]

Additionally Zeeman-GFAAS accessories and instruments are now commercially available especially designed for the direct and practically contamination free analysis of solids (solid sampling).[19,20] This GFAAS mode could be successfully applied for distribution studies of cadmium and other metals in various Reference Material and other materials, i.e. for their homogeneity.[21] Moreover, with appropriate light sources and computerized signal evaluation GFAAS also offers a multielement potential. Thus constituting a promising technique as has been already demonstrated for a number of metals and materials.[22] The attainable detection limits closely approach, even under compromise conditions, that of single element GFAAS.

If flame AAS with Zeeman compensation is used, also this technique can be improved due to a smoother background leading to detection limits that are close to those of Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

Various modes of atomic emission spectrometry with plasma excitation, e.g., inductively coupled and microwave induced plasmas compete with flame AAS. ICP-AES, for example, offers for cadmium a broad multi-element potential and frequently, if more sophisticated instruments (either simultaneous or sequential mode) are used, an effective background correction. Thus, if multielement analysis is required and the concentration of cadmium allows the application of ICP-AES this doubtless is the method of choice, even if the higher investment costs are considered.[6,10,23]

Another, particularly for cadmium very favourable, analytical technique is *Voltammetry*.[6,10,24–26] If differential pulse anodic stripping voltammetry (DPASV) with rotating mercury film electrodes is applied, cadmium can be measured with an extreme detection power down to $\leq 0.2\,\mathrm{ng/l}$ analyte solution. This has been used, if organic compounds are present, after prior UV irradiation, directly in sea water, polar ice and wet deposition (rain and snow) (see also Table I).[25] For cadmium analyses in liquid biological and all solid materials complete decomposition of the interfering organic matter is indispensable. Thus for sample preparation quick and effective decomposition procedures, e.g. wet ashing with an $HNO_3/HClO_4$ mixture,[6,10,24] are necessary. Due to contamination and dilution detection limits in biological material thus regularly are at the order of those obtainable by GFAAS. However, if somewhat elevated cadmium levels have to be determined, e.g. in environmental samples, the very recently commercially offered square wave mode (SWV)[26–28] is particularly advantageous. Since the digestion required for solids in this case need not to be as rigid as for regular DPSAV, often a simple digestion with nitric acid under pressure is sufficient.[6,28] Another advantage is the shortened analysis time of SWV compared to DPSAV if not extremely low levels have to be quantified.[28] Nevertheless, both voltammetric techniques are excellent tools for trace and ultratrace determinations and provide also oligoelement potential.[24] They can be used with satisfactory precision in many duties that range from routine analysis to QC in comparison with other methods.[6,10]

A comparatively new approach in X-ray fluorescence is *Total Reflection X-ray Analysis* (*TXRF*). It became available for practical applications only a few years ago but due to its multielement potential and excellent sensitivity for many elements the number of applications for this method is rapidly increasing. Since it has a good detection power for cadmium (see Table II) it has been already used for this and many other elements in research and surveillance.[29] However, care has to be taken with this method in the presence of interfering matrix elements so it is at its best in aqueous and biological samples.

For special cases, i.e. nondestructive multielement determinations in solids, analytical QC and fingerprint studies *Neutron Activation Analysis* was and still is of benefit in many laboratories all over the world.[6,30] If radiochemical separation after irradiation is applied cadmium can be determined down to very low levels frequently below 1 μg/kg in biological materials.[31,32]

For studies of cadmium accumulation in exposed workers *in vivo biological monitoring*, a particular NAA technique, has been developed; it applies irradiation of liver or kidney with a shielded collimated neutron beam from a ^{238}Pu-Be neutron source. The isotope ^{113}Cd (abundance 12.29%) reacts with slow neutrons to form ^{114}Cd which promptly decays to the ground state in less than 10^{-14} seconds. Detection limits (1.6 mg absolute for kidney and 1.0 μg/g for liver) are sufficient for the intended monitoring task.[33,34]

A precise and accurate method is *Mass Spectrometric Isotope Dilution Analysis* (MS-IDA) with thermal ionization. Despite being a very laborious and time consuming method that requires extreme care in sample pretreatment it offers by far the most reliable data for several elements and thus is frequently used as ultimate checking and reference method in many materials.[6,32,35] Very recently its multielement potential is being evaluated which to some extent can compensate for limitations in time consumption and sample throughput.[36]

ANALYTICAL QUALITY CONTROL

The urgently necessary analytical QC for cadmium can be performed in different ways. Intralaboratory control frequently is achieved by internally characterized samples of known content with a matrix as close as possible to the matrix to be analyzed for cadmium or by comparison of physically independent methods, e.g. AAS-DPASV, SWV; AAS-MS-IDA; TXRF-DPASV; TXRF-ICP-AES; ICP-AES-DPASV etc.[4–6,10] Also the evaluation and application of reference procedures, major aim of IUPAC programmes,[7] and Reference Materials and Certified Reference Materials (RMs, CRMs) is very often necessary. The latter are excellent tools for the development of methods.[6,11] A good selection of different materials is already available or in production for cadmium.[37,38] For special cases also "fresh" materials developed in the frame of Environmental Specimen Banking programmes are in preparation.[39]

Thus, in summarizing it can be stated that there are now various powerful single element, oligo and multielement methods available. They allow in combination with an appropriate QC a proper selection of analytical procedures for nearly all tasks ranging from highest to lowest cadmium contents in numerous biological and environmental materials.

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