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Review

On-line sorption-based systems for determination of cadmium with atomic spectrometry detectors

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ABSTRACT

Determination of cadmium is often required in various environmental, biological and food samples as it is recognized worldwide as a toxic metal. However, these analysis with atomic spectrometry detectors are often difficult due to relatively low content of cadmium and complex matrices. Several preconcentration/separation procedures to determine cadmium have been devised, among them the methods based on sorbent extraction are the most popular. They can be easily implemented and controlled in flow injection (FI) or sequential injection (SI) systems to perform appropriate sample pretreatment. This work reviews the papers, published from 1990, concerning procedures based on sorption principles for on-line determination of cadmium. They were compared using experimental enhancement factor (EF) and concentration efficiency (CE) values.

Contents

1. Introduction

Cadmium is considered in many regards as a significant pollutant because it has been introduced in large quantities into the environment and is highly toxic even at very low concentrations (Robards and Worsfold, 1991). The main contamination sources of this element are anthropogenic: industry wastewaters, mining operations, waste incineration as well as the combustion of some coals and oils. The occurrence of Cd in the environment from natural sources is mainly due to volcanic emissions. Increasing global emission of cadmium compounds into the atmosphere, together with aqueous and solid emission lead to local contamination problems. The epidemiological studies provide increasing

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evidence that this element is carcinogenic and exposure should be controlled to the lowest level possible (Vig et al., 2003). An additional problem of Cd toxicity is its accumulative character. Biological half-time for cadmium in human body is between 10 and 30 years and the critical organ is kidney where one-third of body cadmium accumulates. Cadmium concentrations in urine reflect long-term exposure and its quantity stored in the body (Hotz et al., 1996). The FAO/WHO Joint Committee on Food Additives recommended provisional maximum tolerable daily intake of Cd from all sources (food, water and air) as 1.0–1.2 $\mu g\,kg^{-1}$ body mass (WHO Technical Report, 1972). The maximum permissible level of cadmium in drinking water is 3.0 $\mu g\,L^{-1}$ (Guidelines for Drinking Water Quality, 1998), while cadmium levels in surface seawater samples collected from several beaches in Brazil were in the range of 0.035–0.170 $\mu g\,L^{-1}$ (Ferreira et al., 2004).

Determination of cadmium in environmental and biological materials is an important screening procedure in the studies of environmental pollution and occupational exposure. Cadmium contents in such samples are usually found at trace levels, thus, the analytical methods of high selectivity and low detection limit are required, and frequently a preconcentration step. Spectrometry techniques, including atomic absorption spectrometry (AAS) and inductively coupled plasma emission spectrometry (ICP-OES) as well as inductively coupled plasma mass spectrometry (ICP-MS) are the most commonly used analytical methods for trace cadmium determination. In practice for complex matrices, however, the accurate determination of cadmium is frequently very difficult due to the presence of interfering effects, comprising spectroscopic and non-spectroscopic interferences. Moreover, in some cases, the concentration of an analyte might be to low to be analysed directly, particularly by flame AAS and ICP-OES. Electrothermal AAS (ETAAS) and ICP-MS techniques offer high sensitivities and low limits of detection, but the practical direct application of both methods are often restricted by matrix effects. ETAAS cannot tolerate high contents of salt components and is sensitive to variation in matrix composition (Grotti et al., 1998). Due to the high volatility of cadmium, some difficulties are encountered for its determination, thus restricting the use of a high pyrolysis temperature and the production of concomitant background signals. These difficulties may be overcome to various degrees by applying a powerful background correction or by using chemical modifiers (Garcia et al., 2003; Tsalev et al., 2000; Lima et al., 2002). However, the blanks originating from modifiers, are pronounced and increase limits of detection. The problem with reagent blank levels from several common modifiers used for determination of cadmium was presented by Tsalev et al. (2000).

In ICP-MS, both high contents of matrix salt and organic liquids should be avoided. Non-spectroscopic interferences due to matrix effect can be reduced by sample dilution, but this results in an undesired high limit of quantification which may be further degraded by spectroscopic interferences (Wang et al., 2001). For example, all the useful isotopes of cadmium are overlapped by various isotopes of MoO polyatomic ion (Hwang and Jiang, 1997).

The most effective way to avoid these problems is to perform appropriate sample pretreatment aimed at lowering the limits of detection, by both removal of interferences and increasing the concentration of analyte. Various techniques for cadmium separation and preconcentration have been proposed, including ion-exchange, adsorption, coprecipitation, liquid–liquid extraction and generation of volatile species. The methods which are based on sorbent extraction have proven to be the most attractive ones due to their high separation and preconcentration efficiency. The broad range of choice for sorbent materials along with various chelating reagents and eluents make this technique very attractive for sample pretreatment. Moreover, they can be easily implemented and controlled in the flow systems.

The aim of this review is to present the procedures based on sorption principles, which were used for on-line cadmium determination. They were discussed and compared in terms of selectivity and efficiency as the sample loading mode is an important feature of the flow system. For pure separation purposes, as in the case of interference removal, usually injection of a defined sample volume from a sample loop of a small volume is applied. In flow preconcentration system, the use of longer loading time (increasing sample volume) improves the enrichment, but simultaneously leads to a decrease in the sampling rate. For comparison of the efficiency of the presented flow systems, a concentration efficiency (CE), as the product of enhancement factor (EF) and sampling rate, was applied.

2. Flow systems

Sample pretreatment still remains the bottleneck for a large number of analytical procedures, and often one which could hinders automation and miniaturization. Since the introduction by Skeegs (1957) of the air-segmented flow analysis (SFA), flow systems have proved to be excellent tools for solution handling and consequently for carrying out methods related to wet chemical analysis. As a rule, the aqueous sample is introduced into the analytical path and processed inside it under reproducible conditions. The operational feature of SFA

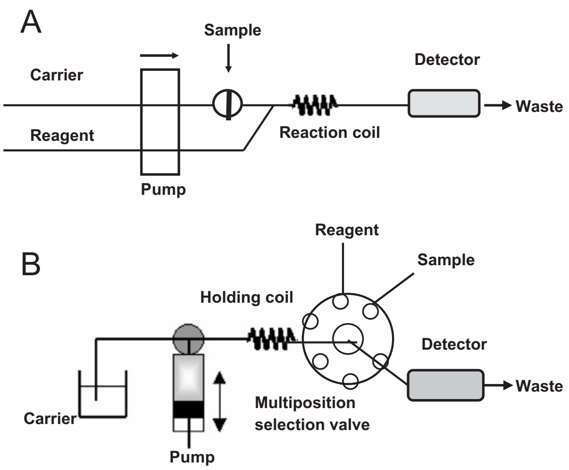

Fig. 1 – Schematic representation of flow injection(A) and sequential injection (B) manifolds.