



# Solvent-assisted dispersive solid phase extraction

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## ABSTRACT

In this research, a novel extraction technique termed solvent-assisted dispersive solid phase extraction (SADSPE) was developed for the first time. The new method was based on the dispersion of the sorbent into the sample to maximize the contact surface. In this method, the dispersion of the sorbent at a very low milligram level was achieved by injecting a solution of the sorbent into the aqueous sample. Thereby, a cloudy solution formed. The cloudy state resulted from the dispersion of the fine particles of the sorbent in the bulk aqueous sample. After extraction, phase separation was performed by centrifugation and the enriched analyte in the sedimented phase could be determined by instrumental methods. The performance of SADSPE was illustrated with the determination of the trace amounts of cobalt(II) as a test analyte in food and environmental water samples by using flame atomic absorption spectrometry detection. Some key parameters for SADSPE, such as sorbent selection and amount, type and volume of dispersive solvent, pH, chelating agent concentration, and salt concentration, were investigated. Under the most favorable conditions, good limit of detection (as low as  $0.2 \mu\text{g L}^{-1}$ ) and repeatability of extraction (RSD below 2.2%,  $n=10$ ) was obtained. The accuracy of the method was tested with standard reference material (SRM-1643e and SRM-1640a) and spiked addition. The advantages of SADSPE method are simplicity of operation, rapidity, low cost, high recovery, and enrichment factor.

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## 1. Introduction

Sample preparation is one of the most important and crucial steps in the whole analytical process, especially when trace determination is the purpose [1,2]. The main aims of this step are: (a) to transfer the analytes to a physical state that enables their analysis and final detection; (b) to enrich the analytes of interest; and (c) to purify the extracts prior to instrumental determination. Several procedures have been developed for these purposes such as liquid–liquid extraction (LLE) [3–5], co-precipitation [6–8], and solid phase extraction (SPE) [9–17]. However, some of these pretreatment methods need large amounts of sample and/or organic solvents, are time-consuming and expensive, and have unsatisfactory enrichment factors. These problems could be addressed by the development of modular and compact processes that provide adequate separation and preconcentration without complex processes.

SPE is more flexible and efficient than LLE in terms of simplicity, low consumption of the organic solvents, flexibility in choosing the adsorbent, and high enrichment factor. Recently, SPE has been increasingly used for the preconcentration and separation of ultra-trace amounts of inorganic and organic species from complex matrices [18,19]. Solid phase extraction techniques are

surface-dependent processes since their efficiency directly depends on the particle size and the surface area of the sorbent [20]. Dispersive solid phase extraction (DSPE) has risen as an alternative to conventional solid phase extraction. It was, for the first time, proposed by Anastassiades et al. [21] and it can be considered as a quick, easy, cheap, effective, rugged, and safe (QuEChERS) sample treatment method. It is based on the SPE methodology, but the sorbent is added to the extract without conditioning, in small amounts (viz. 50 mg) and the dispersion is carried out assisted by an external energy (usually a vortex stirring). The phases are easily separated just by centrifugation. Sorbent dispersion leads to an increase of its active surface, and therefore to an improvement in the extraction kinetics. Moreover, this enhancement allows the use of a smaller amount of sorbent compared to the conventional extraction approaches resulting in the saving of material. In order to obtain analytical information, the sorbent is then recovered after the extraction. The analytes can be directly monitored on the sorbent surface by using a spectroscopic technique [22,23] or can be conveniently eluted/desorbed for the subsequent analysis of the eluted fraction [24–27].

In the present report, for the first time, a novel extraction technique as a high performance and powerful preconcentration method named solvent-assisted dispersive solid phase extraction (SADSPE) is demonstrated. In this method, the appropriate mixture of sorbent and disperser solvent was rapidly injected into the aqueous sample by syringe. Thereby, a cloudy solution formed. The cloudy state resulted from the dispersion of the fine particles of

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the sorbent in the bulk aqueous sample. Then, this cloudy solution was centrifuged, following which the fine particles sediment at the bottom of the conical test tube. The determination of analytes in the sedimented phase was performed by instrumental analysis. In this extraction method, any component in the solution, directly or indirectly after previous derivatization reactions, interacts with the fine particles of the sorbent, and consequently, gets extracted from the initial solution. Simplicity of the operation, rapidity, low sample volume, low cost, high recovery, and high enrichment factor are some advantages of SADSPE. For evaluating the performance of SADSPE, cobalt was selected as a test analyte and determined in food and water samples using flame atomic absorption spectrometry detection. The effects of various experimental parameters on the extraction were investigated.

## 2. Experimental

### 2.1. Apparatus

A PG-990 (PG instrument Ltd., United Kingdom) atomic absorption spectrometer, equipped with deuterium background correction, cobalt hollow cathode lamp and an air–acetylene flame was used for cobalt determination. All data acquisition was made according to peak height with the equipment software. The operating conditions were: wavelength 240.7 nm, spectral resolution 0.2 nm, applied lamp current 5.0 mA, air flow rate 10.0 L min<sup>-1</sup>, and acetylene flow rate 1.3 L min<sup>-1</sup>. A Hettich centrifuge (Model Universal 320 R, Germany) was used for centrifugation. The pH values were measured with a Metrohm pH-meter (model: 827) supplied with a glass-combined electrode. The particle size and the distribution of dispersed sorbent were both determined by dynamic light scattering (DLS) on a Zetasizer Nano ZS (Malvern Instruments Ltd., United Kingdom).

### 2.2. Reagents and solutions

All reagents used were of analytical reagent grade. Ultrapure distilled water was used throughout the experiment. A 1000.0 mg L<sup>-1</sup> stock standard solution of Co(II) was prepared from pure Co (NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O (Merck, Darmstadt, Germany). Prior to the investigations, working standard solutions were obtained by appropriate stepwise dilution of the stock standard solutions.

The all standard solutions for FAAS instrument calibration were prepared in ethanol.

A 0.010 mol L<sup>-1</sup> solution of 1-(2-Pyridylazo)-2-naphthol (PAN) (Merck, Darmstadt, Germany) was prepared in pure ethanol. Naphthalene, benzophenone, and 1,4-dichlorobenzene were purchased from Sigma-Aldrich (Louis, USA). All glass vessels used for trace analysis were cleaned before use by soaking them in 10% nitric acid solution for at least 24 h and then rinsed thoroughly with ultrapure water. A buffer solution (pH 6.0, 1.0 mol L<sup>-1</sup>) was prepared by mixing an appropriate amount of acetic acid with sodium acetate solution. Water standard reference material SRM 1643e (trace elements in water) and SRM-1640a (trace elements in natural water) from National Institute of Standards and Technology (NIST) were both employed to test the proposed methodology.

### 2.3. Preparation of the real samples

Spinach and black tea samples were purchased at a local supermarket. Spinach sample was washed with ultrapure water and cut and oven-dried at 100 °C for 24 h. Next, it was ground in a household grinder. 500 mg of the sample was placed in a 100 mL beaker, and 10 mL of concentrated HNO<sub>3</sub> (65% w/w) was added to the beaker. The mixture was evaporated to near dryness on a hot

plate at about 130 °C for 4 h. After cooling to room temperature, 3 mL of concentrated hydrogen peroxide (30%, w/w) was added. The mixture was again evaporated to near dryness. The resulting solution was diluted to 25 mL with distilled water. Further, the resulting solution was filtered and its pH was adjusted to 6.0 by adding NaOH and 2 mL of acetic acid/sodium acetate buffer solution (pH 6.0). Finally, the solution was diluted to 100 mL with double distilled deionized water. The same preparation procedure was used for the black tea sample. One blank test was performed for each sample. The samples were analyzed immediately after preparation.

All of the collected water samples (tap, mineral, river, and sea water) were filtered through a cellulose membrane filter (Millipore) with a pore size of 0.45 μm, and after their acidification to 1% with concentrated nitric acid, were stored in polyethylene bottles.

### 2.4. Solvent-assisted dispersive solid phase extraction (SADSPE) procedure

50 mL sample or standard solution containing Co(II), PAN (1.0 × 10<sup>-4</sup> mol L<sup>-1</sup>) and acetic acid/sodium acetate buffer (1 mL of 1.0 mol L<sup>-1</sup>, pH 6.0) was poured into a glass screw-cap conical-bottom centrifuge tube. 0.5 mL of methanol solution (as disperser solvent) containing benzophenone (1.0%) (as sorbent) was rapidly injected into a sample solution by using 1.0 mL syringe, and then, the mixture was gently shaken. A cloudy solution was formed in the test tube (the cloudy state was stable for a long time). This cloudy state resulted from the dispersion of fine particles of benzophenone in the bulk aqueous sample. Then, the mixture was centrifuged at 4000 rpm for 5 min. Accordingly, the dispersed fine particles of benzophenone were sedimented in the bottom of the conical test tube. The aqueous phase was then separated completely by a syringe. Later, the sedimented phase was dissolved and made up to 1.0 mL by adding ethanol. The resultant solution was introduced into the flame by conventional aspiration. The extraction steps are illustrated in Fig. 1.

## 3. Results and discussion

There are different factors that affect the SADSPE extraction process namely selection of suitable sorbent, selection of suitable disperser solvent, amount of sorbent, volume of disperser solvent, and extraction time. It is very important to optimize them in order to obtain good recovery, high EF, and low limit of detection.

### 3.1. Selection of sorbent and its amount

Careful attention should be paid in the selection of the sorbent. It should have extraction capability of the concerning compounds, high solubility in disperser solvent and low solubility in water. Naphthalene, benzophenone, and 1,4-dichlorobenzene were compared in the extraction of cobalt(II). A series of sample solutions were studied using 500 μL methanol containing 1.0% of the sorbent. As Fig. 2 shows the highest extraction recovery was obtained with benzophenone. The similarity of the structure of benzophenone and Co(II)–PAN complex and their proper interaction could thus explain the higher extraction recovery of benzophenone. Therefore, benzophenone was selected as the sorbent.

To examine the effect of the sorbent amount, a series of sample solutions were studied using 500 μL methanol containing different amounts (0.2–10.0%) of benzophenone. As Fig. 3 shows, the extraction recovery increased as the amount of benzophenone increased from 0.2 to 1.0%, as was expected. Further increase of the amount of benzophenone to 10.0% did not have any effect on extraction recovery. Therefore, 1.0% of the benzophenone was

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