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Application of probe sonication extraction for the determination of linear alkylbenzene sulfonates from sewage sludge. Comparison with other extraction methods

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ABSTRACT

A new method based on probe sonication extraction (USP) prior to high performance liquid chromatography (HPLC) has been developed for the determination of linear alkylbenzene sulfonates (LAS) from sewage sludge. The optimized method was designed to be cost effective compared to existing extraction methods (ultrasonic assisted extraction, Soxhlet or pressurized liquid extraction) which may require large quantities of organic solvents, or costly instrumentation or equipment.

The main factors affecting the extraction efficiency (extractant volume, ultrasounds power and extraction time) were optimized using compost sludge. The detection limit of total LAS in the sludge was 10 mg kg^{-1}. The extraction of C_{10}–C_{13} homologues is carried out using an extraction time of 7 min with 10 mL of methanol. Liquid chromatography with fluorescence (FL) detector is used for determination of LAS homologues. A mobile phase acetonitrile-water containing 0.1 M $NaClO_4$ (65:35) and isocratic elution was used. Compounds were eluted over 6 min at a flow rate of 1 mL/min. Polar interferences are eluted between 0 and 2 min and no purification of the samples is required prior to the final determination by high performance liquid chromatography (HPLC). The recoveries of LAS in spiked sewage sludge were between 84.0% and 97.0%, which reflect the efficiency of the method for extraction of these analytes from sewage sludge. Concentration levels found were between 11,858 mg kg^{-1} for digested sludge and 2379 mg kg^{-1} for compost sludge.

1. Introduction

Linear alkylbenzene sulfonates (LAS) are the most important synthetic anionic surface-active agents widely used as the principal constituents of commercial detergents. The European consumption of LAS in detergents applications was about 350 kt in 2005. This represents more than 80% of the total European consumption of LAS, which was estimated to be about 430 kt in the year 2005 [1]. They are used as complex mixtures of C_{10}–C_{13} homologues and of positional isomers where the benzenesulfonate is located at various alkyl carbon positions from the second to the center. After application, LAS are usually discharged through the sewage infrastructure to municipal wastewater treatment plants which are subjected to physical and biological treatment. In wastewater treatment plants, 10% or more of the LAS present in wastewater are eliminated by adsorption/precipitation processes [2], together with suspended solids during the primary treatment, while the rest are biodegraded in the aerobic stage of the treatment process. Nevertheless, as a consequence of the low biodegradability of LAS under anaerobic conditions, the sludge that is stabilized by anaerobic processes shows concentrations of LAS as high as 3000–30,000 mg kg^{-1} of dry solid [3–5].

During recent decades a variety of procedures have been used to extract LAS in solid samples. Soxhlet and ultrasounds methods using methanol as extraction solvent are mainly employed [4–7]. Soxhlet and ultrasounds extraction methods are relatively costly, time consuming, labor intensive and require the used of large volume of organic solvents. Some attempts performed in order to reduce both the volume of organic solvents used and the time needed for the complete extraction have been based on supercritical fluid extraction [8] and pressurized liquid extraction with methanol [9,10], all of which require complex and expensive instrumentation. High performance liquid chromatography (HPLC) employing UV or fluorescence detection (FL) is the most frequently used method for the selective determination of LAS [11–15].

The objective of this study was to develop and validate a routine method for analysis of LAS in sewage sludge based on probe sonication extraction (USP) and HPLC-FL determination. The main factors affecting the extraction efficiency were studied and optimized, paying special attention in reducing the volume of organic solvent as well as the time needed for extraction. The method did not require clean-up

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or preconcentration steps and no special equipment is needed. The proposed method has been satisfactorily applied to sewage sludge samples from Seville (Spain) wastewater treatment plant.

2. Materials and methods

2.1. Chemicals and reagents

HPLC grade acetonitrile and methanol were purchased from Merck (Darmstadt, Germany), just as analytical grade sodium perchlorate. Petroquímica Española (Cádiz, Spain) supplied the commercial LAS mixture (Petrelab P-550) with the following homologue distribution: C-10 (12.3%), C-11 (32.1%), C-12 (30.8%), C-13 (23.4%). Standard solutions of LAS were prepared in ultrapure water. Ultra-high-quality water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA).

2.2. Instrumentation

All measurements were made with an Agilent (Palo Alto, CA, USA) 1100 series liquid chromatograph equipped with a fluorescence detector (FL), an injector with a loop 20 μL, a quaternary pump, a vacuum degasser and a thermostated column compartment. The analytical cartridge column was a Zorbax (Agilent) XDB-C8, 150 mm×4.6 mm ID, 5 μm particle size. A C-18 guard column was installed to protect it from contamination. An ultrasound bath Ultrasons-P (Selecta, Spain) was used in ultrasounds bath extraction. Sonoplus ultrasonic homogeneiser (Bandelin, Germany) fitted with a HF generator 2200 and a microtip of 2 mm diameter was used for LAS extraction in ultrasound probe extraction. Centrifugation system was a Sigma k3-15. The microwave extraction system was a Microwave Ethos 900 apparatus (Milestone, Sorisole, Italy) with a programmable power and irradiation time. The apparatus is equipped with a carousel that is able to hold six extraction vessels.

2.3. Sewage sludge collection and preparation

Sewage sludge samples (digested and compost sludge) were collected from Seville (Spain) wastewater treatment plant. Digested sludge is obtained when primary sludge undergoes a process of digestion (aerobic or anaerobic) for its stabilization. 1000 mL of digested sludge were collected in different points to obtain a representative sample. Compost sludge is obtained by exhibition to the sun, with a process of natural fermentation that takes place helped by ventilation. 500 mL of compost sludge were collected in different points of the storage system and different depths to obtain a representative sample. Before analysis, sludge was dried in an oven at 40 °C until humidity <10% (digested sludge between 5 and 7 days and compost sludge between 2 and 3 days) and ground in an agate mortar. The sludge was sieved in order to obtain a fraction <1 mm. This fraction was stored at 4 °C until it was analyzed.

2.4. Preparation of spiked samples

Two portions of 20 g of compost sludge were spiked with commercial LAS at two different concentrations (2000, 4000 mg kg^{-1} of total LAS). One sample was not spiked in order to evaluate the original presence of LAS in sludge. Spiked samples were prepared adding 40

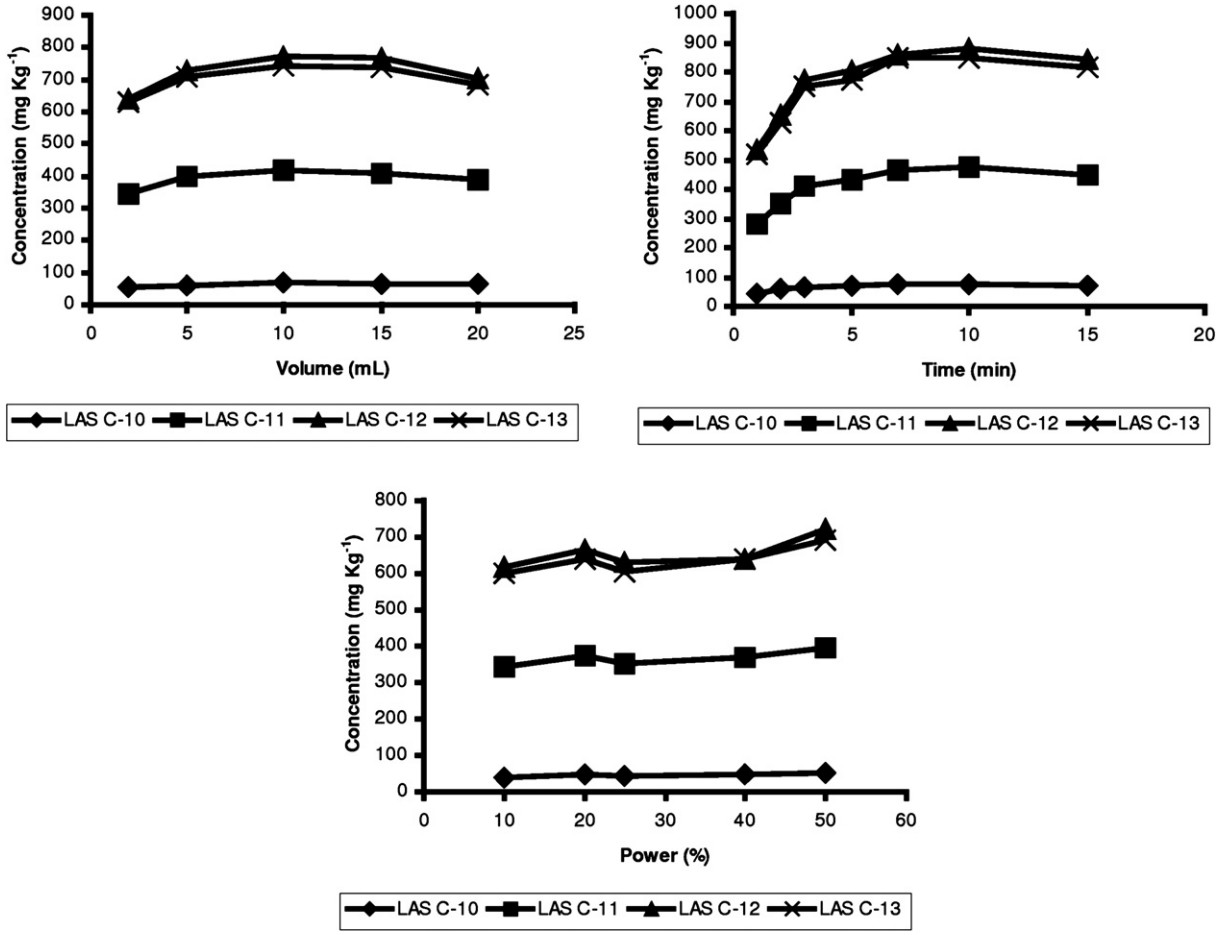

Fig. 1. Optimization of probe sonication extraction (USP).