



A submicron mesoporous silica for the determination of organosulphur in sea water



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ABSTRACT

Organosulphur compounds were determined in seawater samples by gas chromatography using a pulse flame detection method. The analytical method involved the use of octyl-diol mesoporous silica as a replacement for organic solvents in the extraction and pre-concentration of organosulphur compounds from seawater samples based on the solid phase dispersion extraction technique. The detection limits were in the range 0.6–2 ng S/L, while the repeatability and reproducibility were 7–12% and 13–16% respectively. Relative standard deviations (%) for recovery of n-ethanthiol (n-EtSH), di-n-ethyl sulphide (n-Et₂S) and di-n-ethyl disulphide (n-Et₂S₂) in spiked water samples were in the range 2.2–6.6% (at 0.5 µg/L level). Under the experimental conditions used, quantitative extraction of n-EtSH, n-Et₂S and n-Et₂S₂ was achieved with recoveries ranging from 93% to 99%. The procedure has been successfully applied to organosulphur determination in seawater samples collected from Jeddah beach (West of Saudi Arabia).

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1. Introduction

Sulphur like other elements and its compounds are introduced in the environment naturally as well as a form of human activities. It is a widely distributed element in nature and has a number of species present in water bodies. On the other hand elemental sulphur is a common constituent of sediment presenting in anoxic sediment due to biogeochemical and microbiological processes that convert sulphates and sulphides to elemental sulphur [1]. The different sulphur forms that occur in water and bottom sediment can be classified into two groups. (a) Inorganic sulphur forms include sulphates (SO₄²⁻), elemental sulphur (S⁰), metal sulphides (e.g. FeS) and pyrites (FeS₂). In-between the sulphate and the sulphides, several intermediate oxidation state sulphur species are formed, such as bisulphide (S₂⁻, oxidation state-1), thiosulphate (S₂O₃²⁻, +2) and dithionite (S₂O₄²⁻, +3) [2–4]. (b) Organic sulphur forms which, are generally divided into the ester sulphate group and the carbon-bonded sulphur compounds [5,6]. The initial inorganic form of sulphur in natural environment is sulphate, but

sulphide and elemental sulphur are the main forms of inorganic sulphur in nature [7]. These different species are extremely easy to be converted into each other, and even some of them are very unstable and at an extremely low concentration so that they difficult to be detected [8]. The main natural source of sulphur compounds in the environment is volcanic eruptions [9]. Also, sulphur compounds may enter into the environmental sites, such as fresh water and sediment, as a result of human activities. Some of these activities are fossil fuel combustion, the use of fungicides, pesticides, fertilizers in agriculture and in the effluents from the paper industry [8–13]. The naturally occurring sulphur cycle is well known and it has been described in the literature [10,14–16]. Acid rain can be caused by the large pollution of sulphur dioxide and nitrogen oxide [10,17]. They react with the atmospheric water to produce acids. This is the main causes of exceeding safe limits of inorganic sulphur compound concentrations in the natural environment of waters and bottom sediments of lakes, rivers and freshwater reservoirs [18].

Elemental sulphur is non-toxic and considered an essential element. However, the toxicity of sulphur is closely related to its chemical species. High organosulphur concentrations are known to induce cardiovascular illness, Alzheimer's disease, Parkinson's disease, liver cirrhosis and cancer in human beings [19]. Long term exposure of these species even at small quantities increases the health risk [20]. This environmental problems show the urgent

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need for validated procedures which permit selective determination of sulphur speciation at very low level in different environmental samples.

The determination of sulphur compounds in water samples has been a major analytical challenge for a number of reasons: (1) the low level of the analyte (a few ng/g); (2) the limited stability of sulphur compounds in water samples; (3) variability of sulphur levels over the same site due to the tidal cycle; (4) the absence of certified reference materials for water.

Various methods have been reported in the literature for the determination of different sulphur species in aqueous samples including ultraviolet-visible absorption (UV/Visible) [21,22] and electrochemical methods [23,24]. However, the determination of organosulphur compounds was limited. The use of spectrophotometric [25], polarographic [26] and voltammetric [27] methods for the determination of organosulphur compounds has been reported. Also, several reports based on liquid chromatography [28–30] and capillary electrophoresis [31,32] coupled with different detection methods for sulfur speciation analyses have appeared.

Gas chromatography, coupled with element specific detection methods, is widely used for analytical separation, identification and quantification of volatile organosulphur compounds. This is due to its high resolution, low detection limits and its ability to resolve many organosulphur species [33].

Gas chromatography coupled with pulse flame photometric detectors (GC-PFPD) was the most powerful technique introduced for the determination of sulphur species [34]. This is because of the high sensitivity and selectivity that GC-PFPD can provide and it allows the determination of a wide variety of organosulphur species simultaneously [35].

With regard to the progress of extraction techniques, liquid-liquid extraction, which required large amount of toxic organic solvent and time-consuming method, has been replaced by solid-phase extraction (SPE). The SPE requires a lower amount of the organic solvent, but still requires an appreciable amount of hazardous solvents. More recently the extraction and pre-concentration of analytes from aqueous solution has been carried out by solid phase dispersion extraction (SPDE). This method was originally introduced by Anastassiades et al. as a clean-up step [36]. A small amount of solid phase extraction sorbent was initially dispersed in an extract to remove interfering materials and it was then be recovered by centrifugation. Silicas modified with different chemical groups have been used as sorbents in SPDE [37,38].

In 2005, a novel extraction approach based on the SPDE technique was developed by Howard and Khadry [39] that employed carefully size-selected modified Stöber-type spherical silica particles functionalized with different chemical groups (extracting agent). The idea of this method is based on the partitioning of the analyte between a submicron solid and a liquid phase as a colloidal sol. By tailoring the size of the particles to approximately 250 nm diameter, they can be easily dispersed in aqueous solution, without the need for any mechanical or hand shaking and the solid can then be readily recovered, together with the analytes, by simple filtration or centrifugation [40].

The aim of this paper is to develop a simple, rapid, sensitive and accurate method of speciation analysis of organosulphur compounds in natural water samples using GC-PFPD. The whole procedure (derivatization plus extraction plus quantification) takes less than 30 min, and allows the determination of organosulphur compounds simultaneously at the low ng levels. The analytes are first derivatized in aqueous solution using sodium tetraethylborate and the alkylated products were extracted using the submicron mesoporous silica and then selectively determined by GC-PFPD.

2. Materials and methods

2.1. Materials

All reagents and acids were of analytical reagent grade unless otherwise stated. Glasswares were decontaminated by immersion for 24 h. in 10% HCl solution. After that they were rinsed several times with deionized water. Deionized water (>14 MΩ cm) was purified by reverse osmosis, followed by deionization using an Elga Option 4 system. Toluene was HPLC grade (99.8%), dried by fractional distillation under N₂ from over phosphorus (V) oxide P₂O₅. Hydrochloric acid (37%, laboratory grade), sodium acetate (anhydrous, 99%), ammonia solution (SG = 0.88, 35% (w/v)) and glacial acetic acid (99.99%) were obtained from Fisher (UK). (1-Dodecyl) trimethylammonium bromide (C₁₂TMABr, 99%) was purchased from Alfa Aesar (Lancashire, UK). Tetraethoxysilane (TEOS, 98%) was obtained from Aldrich (Dorset, UK). Octyltriethoxysilane (CH₃(CH₂)₇Si(OC₂H₅)₃) ≥97.5%, n-ethanthiol (EtSH, 95%), di-n-ethyl sulphide (n-Et₂S, 98%), di-n-ethyl disulphide (n-Et₂S₂, 99%), di-n-butyl disulphide (n-Bu₂S₂, 97%) and glycidoxypropyltrimethoxysilane (GMOS, 98%) were obtained from Sigma–Aldrich (Gillingham, UK). Sodium tetraethylborate (NaBEt₄, 97%) was purchased from Acros Organics (UK) and was kept in a glove box under a nitrogen atmosphere to prevent its degradation by atmospheric moisture. The 1 M pH 5 buffer solution (acetic acid/sodium acetate) was prepared by mixing 21.4g of sodium acetate with glacial acetic acid in 250 mL deionised water until a pH of 5 was obtained.

2.2. Instrumentation and conditions

All analysis were performed with a Varian 3800 gas chromatograph (Walnut Creek, CA, USA) that was equipped with a pulse flame photometric detector (PFPD) and a Varian 1079 Programmable temperature vaporizing (PTV) injector. An auto injector unit was used to introduce the prepared solutions/samples. Splitless injection of 1 μL was performed, with a split delay of 1 min and a split ratio of 50. The GC separation was carried out using a non-polar capillary column [Sigma–Aldrich, SA-1 type, fused-silica 30 m × 0.25 mm, coated with non-polar stationary phase polydimethyl-siloxane (PDMS, 0.25 μm film thickness)]. Nitrogen was used as the carrier gas (flow: 1 mL/min). The detector was fitted with a high transmission band filter (320–450 nm; GB 12) and operated at 250 °C. Gas flow rates were: Air1 17.0 mL/min, Air2 10.0 mL/min and H₂ 13.5 mL/min. The flame ignition frequency was ca. 2.6 Hz. The detector gate settings were 3 ms delay and 3 ms width. The operating conditions used for the gas chromatographic determination of organosulphur compounds are summarized in Table 1.

2.3. Standard solutions preparation

For sulphur compounds solutions, ethyl sulphides (n-EtSH, n-Et₂S and n-Et₂S₂) stock standards were prepared at a concentration of ca.

Table 1
Operating conditions of GC-PFPD.

Parameters	Conditions
Column	Sigma–Aldrich, SA-1 type, fused silica-30 m × 0.25 mm × 0.25 μm
Carrier gas	Nitrogen
Injector temperature programme	150 °C (1 min hold), to 250 °C at 40 °C/min
Oven programme	50 °C (3 min hold), to 100 °C at 30 °C/min, to 130 °C at 7 °C/min, to 270 °C at 11 °C/min, hold 13 min.
Make up gas flow rate	1.00 mL/min

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