Removal of sulfur from a solvent extract

Agata Mechlińska, Lidia Wolska, Jacek Namieśnik

The presence of sulfur in a solvent extract that is to be analyzed chromatographically impairs and sometimes precludes proper interpretation of the chromatogram, as the sulfur peak masks the peaks of other compounds present in the sample, and sulfur also disrupts the operation of the mass detector. This means that discrepancies in the results can lead to erroneous interpretations and false assessments of environmental risk. For this reason, sulfur should be removed from an extract prior to chromatographic analysis and determined in a separate analytical run using an appropriate procedure.

This article presents a critical analysis of known methods for removing elemental sulfur from solvent extracts prior to the final determination step of chemicals in the group comprising polychlorinated biphenyls, polyaromatic hydrocarbons and polybrominated diphenyl ethers.

Keywords: Chromatographic analysis; Desulfurization; Persistent organic pollutant; Polyaromatic hydrocarbon (PAH); Polybrominated diphenyl ether (PBDE); Polychlorinated biphenyl (PCB); Sediment; Soil; Solvent extract; Sulfur

Agata Mechlińska*,
Lidia Wolska, Jacek Namieśnik
Department of Analytical
Chemistry, Chemical Faculty,
Gdansk University of
Technology (GUT),
11/12 G. Narutowicz Str.,
80-233 Gdańsk,
Poland

Medical University of Gdansk,
Interdepartmental Institute of
Maritime and Tropical
Medicine, Department of
Environmental Toxicology,
Powstania Styczniowego Str.
9b, 81-519 Gdynia,
Poland

1. Introduction

Elemental sulfur is present in samples whose organic constituents have been subjected to the action of microorganisms. This situation may apply to environmental media (e.g., water, soil, and sediments) or industrial and communal wastes. Sulfur is present in the environment in oxidized, reduced or native form, and is subject to continual change (the sulfur cycle) [1].

Sulfur can enter the aquatic environment as [2]:

- gases (e.g., SO_2, SO_3),
- liquids (e.g., sulfuric acid or salt solutions), and,
- solids {e.g., elemental sulfur or sulfides [e.g., pyrite (FeS_2), chalcopyrite ($FeS*CuS$) or pyrrhotite (FeS)] and/or sulfates [e.g., gypsum ($CaSO_4*2H_2O$) or barite ($BaSO_4$)]}.

In bottom sediments, it is principally the inorganic forms of sulfur that are deposited (i.e. sulfates, elemental sulfur and metal sulfides). Being insoluble in water, elemental sulfur is the form usually occurring in sediments, so it constitutes a serious threat to living organisms [3]. The most common form of sulfur in sediments is octahedral sulfur (S_8), which has a molecular mass of 256 Da. The retention parameters of octahedral sulfur are much the same as those of polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). Schubert et al. [4] and Billon et al. [5] therefore recommended removing it prior to the final determination step, but, unfortunately, this is not an easy task.

When solvent extraction is applied, the usual technique for extracting PAHs and PCBs, sulfur is co-extracted with the sample. The presence of sulfur in a solvent extract that is to be analyzed chromatographically hinders, and sometimes renders impossible, the proper interpretation of the chromatogram, as the sulfur peak masks the peaks of the other compounds present in the sample. That means that the results show discrepancies, which can lead to erroneous interpretations and false assessments of environmental risk [6]. Analytical problems also occur with respect to the appropriate means of removing sulfur and the amount of ''material'' used for this clean up.

As an example, Fig. 1 shows chromatograms obtained during analysis of PCB-group chemicals of solvent extract of the sediment sample using a GC-MS technique. Fig. 1A shows the chromatogram obtained prior to elimination of the elementary sulfur while Fig. 1B shows the chromatogram obtained after elimination

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*Corresponding author.
E-mail: chemanal@pg.gda.pl

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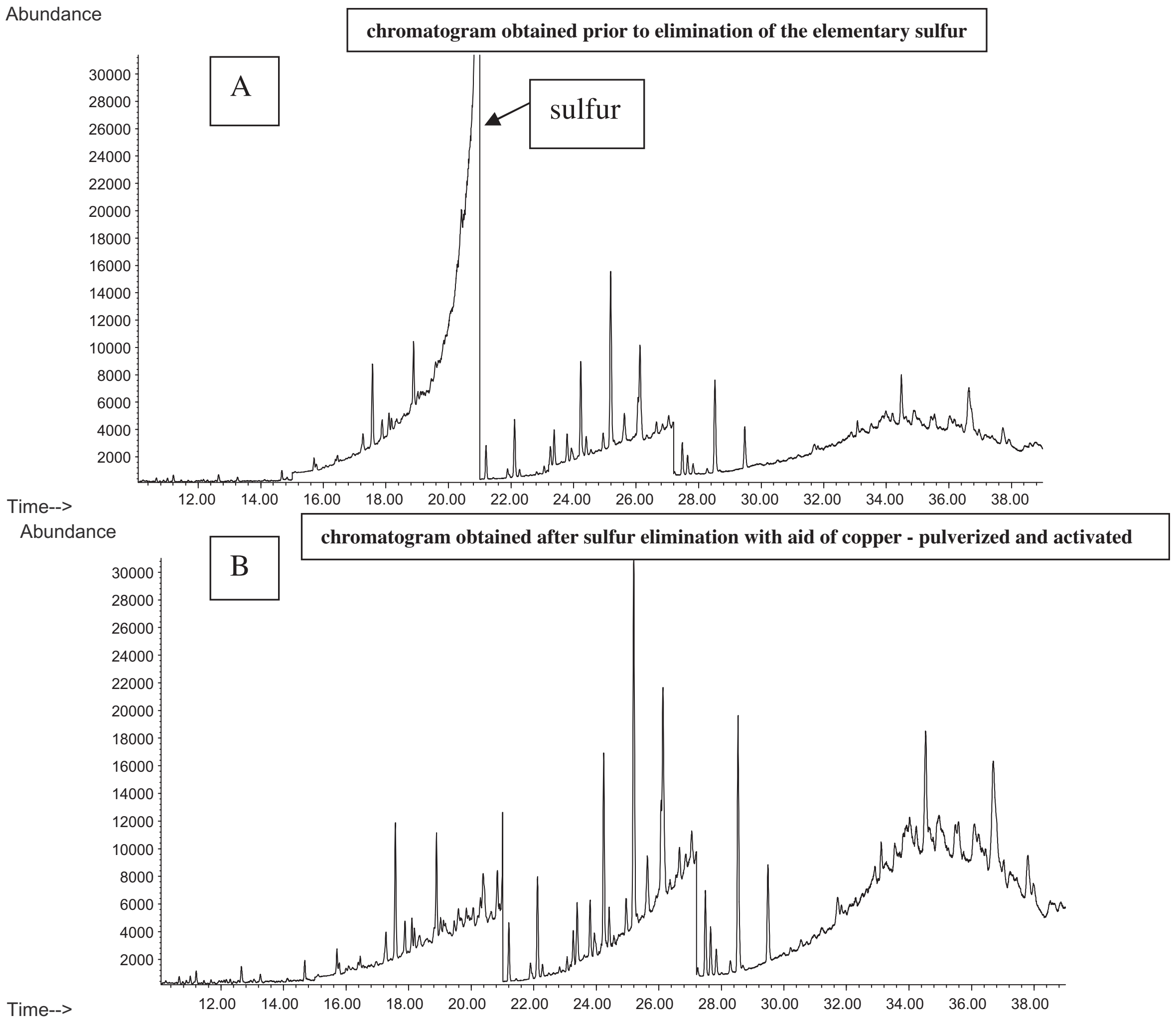

Figure 1. Chromatograms obtained during analysis of PCB-group chemicals of solvent extract of sediment sample using a GC-MS technique: (A) chromatogram obtained prior to elimination of the elementary sulfur; and, (B) chromatogram obtained after elimination of sulfur (S8) using copper, pulverized and activated prior to removal.

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Moreover, brochures published by the manufacturers of monitoring equipment [6,7] mention that elemental sulfur should not be allowed to get into a GC-MS system because it may disrupt the operation of the mass spectrometer, which is usually the type of detector used nowadays. For this reason, sulfur should be removed quantitatively from an extract prior to chromatographic analysis and determined in a separate analytical run using an appropriate procedure.

2. Clean up of solvent extract

The clean up of a solvent extract is of great significance for the entire analytical procedure. The principal task of this step is to remove undesirable compounds that interfere with the identification or the quantitative determination of target analytes. This step can be omitted in determination of contaminants in samples with a fairly simple matrix composition and small organic load [8]. But samples of bottom sediments or suspended matter, whose matrices have a very complex physicochemical structure, require a clean-up step, during which constituents undesirable from the analytical point of view should be removed, e.g. [6,9]:

(1) polymolecular, non-volatile compounds (e.g., fats and waxes) with molar masses of the order of 600–1500 g/mol, containing polar functional groups able to form hydrogen bonds;
(2) compounds with a molecular mass roughly the same as that of the contaminants to be determined, eluted primarily from washers and tubes and other parts of apparatus made from synthetic materials (phthalates and siloxanes), and compounds