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Journal of Chromatography A, 793 (1998) 1–19

JOURNAL OF CHROMATOGRAPHY A

Review

Problems with the determination of environmental sulphur compounds by gas chromatography

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Received 30 December 1996; received in revised form 17 September 1997; accepted 24 September 1997

Abstract

The occurrence of environmental sulphur species, which are significant biogenic and antropopogenic pollutants of the atmosphere, and some problems with their gas chromatographic determinations are reviewed. Techniques most frequently applied for their sampling from gas and liquid matrices, as well as preconcentration or isolation methods are discussed. The problems encountered in chromatographic analysis of sulphur-containing compounds, including chromatographic columns and detection systems, are also described. The simple procedures of avoiding the losses and transformations of these compounds during storage, sampling and analysis (e.g., oxidant removal, silanization) are briefly presented. © 1998 Elsevier Science B.V.

Keywords: Reviews; Environmental analysis; Sample handling; Trace analysis; Sulphur compounds, volatile

Contents

0021-9673/98/$19.00
PII S0021-9673(97)00997-7

1. Introduction

Over the last two decades there has been an increasing demand for the determination of volatile sulphur compounds in the environment. This attention towards these compounds is due to:

(1) *Environmental concern*. Volatile sulphur compounds constitute a significant source of biogenic and anthropogenic atmospheric pollution and therefore they can be responsible for environmental damage including acid deposition, rapid acidification of lakes, the loss of forests, the corrosion of metal structures and historical monuments [1–13].

(2) *Role in global chemical cycles.* Dimethyl sulphide (DMS), a prevalent sulphur compound in sea water, produced in the oceans, is believed to play a critical role in the global sulphur cycle and the radiation balance of the Earth [14–17]. Also, other sulphur compounds may contribute significantly to the sulphur flux in the atmosphere.

(3) *Taste and odour problems*. Some of these compounds – though present at trace levels in different waters, foods, beverages and fragrances – are responsible for taste and odour [18–22]. They are also the source of malodorous conditions in municipal sewage systems [23–25].

(4) *Quality of petroleum and chemical products*. In petrochemical and chemical applications even trace levels of sulphur impurities may cause concern because they can poison the catalysts, impart undesirable properties to final products or produce general air pollution when fuel is burned [26–29].

Therefore, the determination of total organic sulphur, particular classes of sulphur compounds (thiols, sulphides, etc.), as well as individual components (speciation analysis) is of constant concern in many fields.

This review will focus on the six most abundant biogenic sulphur compounds such as hydrogen sulphide (H_2S), carbonyl sulphide (COS), dimethyl sulphide (DMS), dimethyl disulphide (DMDS), carbon disulphide (CS_2) and methanethiol (methyl mercaptan). These compounds have received a great deal of attention because of supposition that the emission of natural sulphur compounds may be substantial even compared to anthropogenic sources of sulphur dioxide. Frequently, all these compounds are called reduced sulphur compounds (RSCs). The emphasis will be especially put on DMS which is a predominant form of volatile sulphur compounds in the oceans.

2. Occurrence of volatile organic sulphur compounds in different environments. Natural and man-made sources

Volatile sulphur compounds (VSCs) are released into the atmosphere by various natural and anthropogenic sources. At preindustrial times, about two centuries ago, anthropogenic emissions of sulphur gases (including biomass burning) were almost negligible and the sulphur cycle was controlled by natural emissions only. Since the beginning of the last century, due to human population growth and general industrialization, a substantial increase of anthropogenic sulphur emissions has taken place, amounting to about a three-fold on the global scale [6]. Recently, both sources are comparable in some aspects. For example, DMS entering the atmosphere from the oceans may add sulphur at the concentration roughly equivalent to the input from sulphur dioxide derived from fossil fuel combustion [30].

The man-made sources of sulphur species emission are relatively well known and allocated.

The main anthropogenic source of volatile sulphur compounds is fossil fuel burning. Also, petrochemical and pulp and paper industry, municipal sewage systems, ore smelting and spillage of oil may be important sources of these com pounds. The wastes from oil refineries contain sulphides and thiols at the level from sub to several mg/dm^3 [31]. Larger amounts of organic sulphur compounds are found in wastes from plants converting coal into coke [31]. Pulp and paper industry constitutes an important source of these compounds, emitting beside sulphates such compounds as hydrogen sulphide, methyl mercaptan, dimethyl sulphide and disulphide [32]. The annual man-made sulphur emission to the atmosphere falls into a relatively narrow range of about 93 ± 15 Tg (S) (2.9 ± 0.47 Tmol) which is 41% of the total emission of this element [33,34]. These data have an averaged character because the amount of anthropogenic emission strongly depends on the Earth region. In the Northern Hemisphere, where industrial activities are greatest, anthropogenic emis-

sions account for 56% of the total sulphur emission; whereas in the Southern Hemisphere they are only 8% [1]. In contrast, the characteristics of the natural biogeochemical sulphur cycle in the atmosphere/biosphere/ocean, are much less known. Furthermore, the form of sulphur emissions is quite different. In contrast to anthropogenic emissions, which are almost entirely in the form of SO_2, the natural emissions are predominantly in the form of reduced sulphur compounds. Recently, these compounds have received an intense interest because of their potential involvement in the regulation of global climate [17,35,36].

The main biogenic sources of sulphur emission are the oceans, freshwater wetlands and wetland soils, living plants, biomass burning and volcanoes. A summary of natural sulphur emissions from all the sources were recently presented [37,38]. In spite of the fact that estimates of these fluxes are based on current information, most estimates are rather uncertain. Due to technical problems and difficulties in the determination of various sulphur species and particularly the emission of particulate sulphur in the form of dust and seaspray, emissions from soil and plants may be uncertain. Recent data depicted lower emissions rates from terrestrial ecosystems making the oceans and fossil fuel burning by far the most important sources of atmospheric sulphur. Emissions from plants are now considered as being at least as important as soil emissions. A detailed discussion of biogenic sulphur cycle and sulphur fluxes over tropical continents has been given by Andreae and Andrea [39].

Natural volatile sulphur compounds emitted into the atmosphere originate from the reduction of sulphate, a predominant form of sulphur in aerobic waters and soils. Biochemical reduction can be considered as the driving force of the atmospheric sulphur cycle. The major pathways of the biogeochemical sulphur cycle were given by Jaeschke et al. [40]. Biochemical reduction of sulphate can proceed by two pathways: assimilatory and dissimilatory reduction. The first way leads to incorporation of sulphate into such biomolecules as cysteine and methionine used as food by living plants and marine algae. Next, reduced sulphur species are released as a consequence of decomposition processes [41] and active release mechanisms of living plants [42]. In dissimilatory reduction, sulphate-reducing bacteria (*Desulfovibrio, Desulfotomaculum)* reduce sulphate and other sulphur oxides to support respiratory metabolism, using sulphate as a terminal electron acceptor instead of molecular oxygen. This process occurs in anoxic sediments of aquatic ecosystems and in anoxic soils and is considered as the major pathway for the global production of H_2S.

Once in the atmosphere reduced, sulphur compounds are photochemically oxidised by OH or possibly NO_3 radicals. The major products of these reactions are thought to be methane sulphonic acid (MSA) and SO_2 which in turn may be oxidised to sulphate [43]. The mechanism of the oxidation of short-lived S(-II) compounds has been extensively studied [44–48]. The finally produced sulphate reenters the biosphere by wet and dry deposition. MSA and sulphate are incorporated into the atmospheric aerosols which seem to be a major contributor to acidity in remote marine areas and may act as cloud condensation nuclei with possible climatic consequences [49,50].

3. Determination of volatile sulphur compounds

The procedures most frequently applied for determination of volatile sulphur compounds in gases and liquids are shown in Fig. 1.

The analysis of volatile sulphur compounds in different environmental matrices is still a big challenge for the analytical chemist. The main difficulties in their determinations result from:

(1) *General problems encountered in environmental analysis*. Most of these compounds are present at low concentrations, frequently at the low parts per trillion (ppt) level. They may be encountered in very complex matrices and in a broad range of concentrations (often several orders of magnitude). Complex mixtures can cause interference problems between major and minor constituents.

(2) *Highly reactive nature of sulphur compounds*. It is well known that these compounds have absorptive, adsorptive, photooxidative and metal catalytic oxidative features [51–54]. This can lead to irreversible adsorption, reaction with each other, catalytic reactions, rearrangements catalysed by different ma-

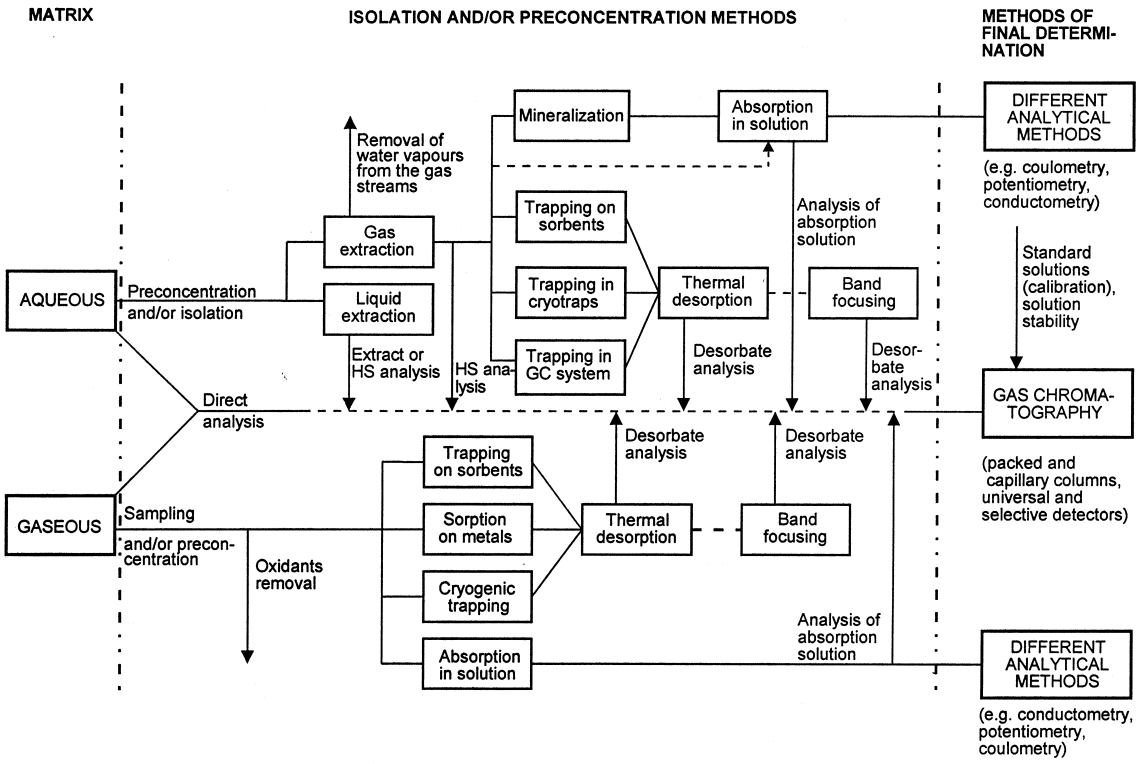

Fig. 1. Procedures most frequently applied for determination of volatile sulphur compounds in gases and liquids.

terials and reactions with substances they come in contact.

Due to these reasons special precautions should be taken during all steps of their analysis, e.g., during sample treatment (sampling, storage, preconcentration and isolation) as well as during the analytical process (gas chromatography in this case).

Direct analysis of reduced sulphur compounds, preferred as quicker and easier to perform, is generally impossible due to their low concentration, typically less than the ppb level. These concentrations are frequently below the direct quantification limits for most of the current methods. Therefore, a preconcentration or/and isolation step must be included in the analytical procedure, complicating the analysis of these compounds. The majority of current analytical methods employ separation as well as preconcentration in order to get qualitative and quantitative information.

Successive paragraphs will present some problems encountered in all steps of their analysis, e.g., during sampling, preconcentration, isolation and detection.

3.1. Sampling procedures from gaseous and aqueous matrices

3.1.1. Sampling from gases

Volatile sulphur compounds in air are collected in all types of vessels such as glass sampling bottles or bulbs, different canisters and polymer bags [55,56]. In order to minimize the adsorption losses and to avoid possible reactions the materials used should be as inert as possible. All materials in sampling vessels, tubing and nuts contacting the sample should be carefully chosen. For the same reasons, vessels have to be conditioned or covered with inert materials prior to use. Glass sampling bottles or bulbs are commonly used for collecting and transporting gas samples or to blend a calibration gas mixture [57]. Stainless steel canisters and PTFE bottles are very

convenient [58]. Frequently, the canisters are conditioned by heating under vacuum before use. Especially, silanization of all parts of vessels which can be in contact with sampling materials is highly recommended. Sampling bags made of Tedlar films which is a polyvinylfluoride (PVF) are chosen because of their simplicity and inertness [59–61]. To prevent losses of sulphur compounds, sample inlets are masked with Al foil to avoid photochemical reactions [62].

Analysis of VSCs in air is complicated by the presence of atmospheric oxidants which can cause variable and often severe sampling losses of these compounds. Different scrubbers are recommended to remove such oxidants as SO_2, O_3, NO_x and others. A number of scrubbers for oxidant removal including PTFE and Tygon shavings, and various substrates (glass fibre filters, Chromosorb, Anakrom, and glass beads) coated with Na_2CO_3 or MnO_2 were evaluated [63]. The Na_2CO_3 based scrubbers appeared to give good results and were used in field studies [64,65]. Comparison of the carbonate-based Anakrom scrubbers and the KOH filter showed that latter scrubber revealed rapid losses of efficiency [66]. Bates et al. [67] and Ayers and al. [68] removed oxidants by a prefilter impregnated with potassium or sodium hydroxide. Kittler et al. [69] reporting the results of an intercomparison of the various oxidant scavenging methods found the KI/glycerol/Vitex filter to be superior to the filter scrubbers using Na_2CO_3 and KOH/NaOH. The recommended scrubber should be stored under absolute air-tight and dark conditions. Davison and Allen [70] have investigated several oxidant scrubber materials. They found that in-line scrubbers utilizing Na_2CO_3, $FeSO_4 \cdot 7H_2O$, KI or KBr, either pure or coated on a chromatographic support (Anacrom P) were ineffective for oxidant removal in moderately polluted air. KI scrubbers were, however, effective for use in clean remote marine air. Their method developed for DMS measurements in polluted air is based on a prolonged contact of the air sample with a KI/NaOH solution. Ivey and Swan [71] passed the sampling air for DMS and CS_2 determination through a potassium iodide coated oxidant scrubber contained in a polycarbonate filter holder. A prefilter with a 2% KI solution and potassium dihydrogenorthophosphate was also used as oxidant remover [72]. A high-capacity, easy to prepare and store, dry and absolutely harmless scrubber system based on 100% cotton wadding was recently proposed [62].

Due to low concentration of sulphur species in air samples, different preconcentration techniques are applied before the analysis proper. The most frequently used methods for these purposes are:
– Sorption on certain metals
– Sorption on solid sorbents
– Cryogenic trapping

3.1.1.1. Sorption on metals

This preconcentration method is based on the ability of certain metals (mainly gold, palladium and platinum) to chemisorb sulphur gases [35,63,73,74]. Some authors describe the application of glass or quartz tubes filled with gold wool [70,75,76], gold-coated glass beads [63], gold-plated sand [63] or metal foils [77]. The wool preparation procedure was described by Kittler [69]. Farwell et al. [77] pulled a sample through a PTFE cell containing a thin metal foil of palladium (Pd) platinum (Pt) or gold (Au). Custom-fabricated Pd on Pt takes advantage of the analytical collection efficiency of Pd and the increased durability and lifetime. In the next step, a large, controlled current is passed through the foil, rapidly desorbing chemisorbed sulphur compounds back into a gas phase. Such a technique – metal foil collection/flash desorption and flame photometric detection – has demonstrated a detection limit for the total sulphur concentration of around 10 ppt (v/v) (pptv) [78].

Generally, it is difficult to evaluate the method because the breakthrough volumes and recovery data have not been reported.

3.1.1.2. Sorption on solid sorbent

Adsorption on solid sorbents is one of the simplest and most efficient methods of concentration of volatile compounds. Adsorbent trapping is very popular, especially when traps are kept at low temperatures. Ambient temperature trapping may frequently give poor recoveries due to poor collection efficiency.

Many sorbents, such as activated charcoal, silica gel, aluminium oxide, graphitized carbon black, molecular sieves and porous polymers were applied to collect volatile sulphur species. The use of porous

polymers is the most widespread due to its ease of use. First of all, the collected substances can be desorbed from porous polymer much easier, compared especially with desorption from charcoal. Furthermore, collection efficiency on porous polymer is less sensitive to the water vapour in sampling atmosphere. The trapped compounds are usually freed by heat desorption and injected into a GC column. Sometimes before this operation, they are once more cold-trapped in a capillary in order to focus their zones.

Among the porous sorbents, Tenax has received the highest popularity [79,80]. Tenax has a low affinity for water and breakthrough volume is relatively independent of humidity. It is well suited for thermal desorption techniques as it exhibits high thermal stability (375°C) and can be subjected to repeated temperature cycling without deterioration. The determination of several sulphur gases can be easily conducted, even though Tenax has a relatively low specific surface area (ca. 19 m^2/g) which as a consequence limits the sampling volume.

An essential step in the selection of a suitable sorbent for preconcentration of VSCs is knowledge of its adsorption capacity by determining the breakthrough volumes (BTVs). Several investigations of sorption of organic sulphur compounds have been carried out. One of the earliest was the trapping of methanethiol, DMS and DMDS on silica gel at −78°C [81]. A systematic work involving the determination of the BTVs of eight thiols, two sulphides and one disulphides on nine porous polymers and on Carbosphere was carried out by Torres et al. [82]. Their paper does not list breakthrough volumes exceeding 15 dm^3/g of sorbent. Cole [83] reported the preconcentration of thiols, disulphides and isothiocyanates on Porapak Q and Tenax GC. Collection of reduced sulphur compounds, COS, H_2S, MeSH, CS_2, DMS and DMDS in traps packed with molecular sieve 5A and Tenax GC has been reported by Steudler and Kijowski [84]. Przyjazny [85] determined the breakthrough volumes for vapours of eleven organosulphur compounds (thiols, sulphides, disulphides, thiophenes) on selected porous polymer (Chromosorb 102, XAD-2, XAD-4, XAD-7 and Tenax GC). The values of BTVs (dm^3/g) extrapolated to 20°C are listed in Table 1. On the basis of the breakthrough volumes, the most suitable sorbent for preconcentration of highly volatile organosulphur compounds was XAD-4. Actually, due to bleeding and efficiency problems, this sorbent is not widely used for collecting sulphur compounds.

Reduced sulphur compounds are strongly adsorbed on molecular sieve 5A which allows large BTVs enabling noncryogenic trapping of these compounds from atmospheric samples. Molecular sieve 5A recommended by Black et al. [86] was successfully applied as a trap for sampling of different sulphur gases [23,70,87]. Multi sorbent trapping (Tenax TA, Chromosorb 106 and Spherocarb) after purging

Table 1
Breakthrough volumes of some sulphur compounds on selected sorbents [85]

Compound	Breakthrough volume (dm^3/g)					
	Concentration (ppm, v/v)	Chromosorb 102	XAD-2	XAD-4	XAD-7	Tenax GC
DMS	0.70	4.7	2.9	10.1	4.4	0.47
DES	0.87	173	52	8600	304	9.9
Di-*n*-propyl sulphide	1.0	3140	50000	>100000	36900	9.9
Diisopropyl sulphide	0.22	139	26800	15900	159000	15.1
DMDS	1.6	76	35	51	84	17.9
DEDS	6.6	1110	290	>61	150	139
Thiophene	11.5	35	28	622	332	26
2-Methylthiophene	1.0	71	79	1530	404	27
MeSH	7.9	0.79	0.45	1.3	0.75	0.29
EtSH	7.3	4.8	2.7	24	3.6	0.97
PrSH	13.5	4.8	3.7	19	6.1	1.6

volatile organic compounds from sediments (MeSH, CS_2, DMS, DMDS, propanethiol, thiophene and 3-methylthiophene among them) was used by Bianchi et al. [88]. Tangerman [89] tested Tenax tubes for some sulphur volatiles at room temperature and at −196°C. At ambient temperature, the trapping efficiency of Tenax TA was not sufficient to retain the low boiling organic sulphur compounds that were present in the samples. More efficient was cooling the trap to the temperature of liquid nitrogen but this created a problem when excessive amounts of methane were present in a sample. Cooling with solid carbon dioxide was found [90] to be suitable for efficient trapping of VOS compounds eliminating the methane coadsorption. The obtained breakthrough volumes are given in Table 2. In the same Table the values obtained by Shooter et al. [91] on the same sorbent are also presented. Small Tenax TA traps (0.08 g) cooled electrically to 15°C (based on Peltier effect) were used to collect natural sulphur compounds [92]. The electric cooling which requires no cryogen is more suitable for field studies. The same sorbent was used as packing of the liner of PTV injector. First, the sample of air was collected by connecting the liner packed with Tenax TA to an air sampling pumping system [93,94]. Next, the sulphur gases were released according to programmed temperature from the adsorbent.

Carbosieve adsorption tubes have been successfully used for collecting CS_2 after purging it from the seawater samples [95–97].

Recently, Devai and Delaune evaluated fourteen solid sorbents for sampling trace levels of carbonyl sulphide and methanethiol [98,99]. These species were separated from other collected reduced sulphur compounds (H_2S, CS_2 and DMS) and analysed using a thermal desorption–gas chromatographic method. The best sorbents for trapping these compounds from dry atmosphere were: silica gel (recovery for COS 90.3%, for MeSH 96.4%), Carbotrap 301 (recovery for COS 99.7%) and molecular sieve (recovery for MeSH 86.2%). For moist samples (96% relative humidity) acceptable recoveries were observed for following sorbents: silica gel (recovery for MeSH>95%), molecular sieve (recovery for MeSH 73.9% for COS 75%) and Carbosieve III S (recovery for COS 71.7%) used along with calcium chloride as a drying agent. For methanethiol recovery values showed no significant changes during 36 h storage or using different flow-rates in the range of 10–80 cm^3/min [98].

3.1.1.3. Cryogenic trapping

Cryogenic trapping is the technique of choice for collecting VSCs from air samples [8,24,48,62, 65,71,89–91,100–111], but is not always practical due to transportation and storage difficulties (at remote locations).

The cryogenic traps (sampling loops) are generally either U-shaped or straight tubes and they can be open or packed. Some packing materials such as glass-fibre wool, glass beads, Tenax, Porapak Q and activated carbon have been used as packing of cryogenic traps. PTFE, borosilicate glass and quartz are the most popular materials for cryogenic traps. Typical dimensions of such traps are as follows: length 8–30 cm, I.D. 3–4 mm and O.D. 4–6 mm. During sampling the traps are most frequently im-

Table 2
Breakthrough volumes of some sulphur compounds on Tenax traps [89,91]

Compound	Breakthrough volume		
	by Tangerman [89] (dm^3/200mg)		by Shooter et al. [91] (dm^3/g)
	Room temp.	−196°C	Room temp.
H_2S	0.004÷0.015	>40	0.08
SO_2			8.00
COS			0.24
CS_2			4.6
DMS	0.55÷1.3	>40	3.8
DMDS	>1	>40	
MeSH	0.10÷0.21	>40	0.54
EtSH	0.45	>40	

mersed in liquid nitrogen (−196°C), or in liquid argon (−186°C). Using the latter cryogen avoids the condensation of oxygen. A mixture of cryogen and methanol or ethanol, solid carbon dioxide or suspension of solid carbon and compressed air were also used for this purpose. The trap for collecting DMS from 200 ml of air was also cooled electrically to 15°C [92]. The frozen compounds are frequently volatilized via heating using hot water.

The cryogenic trapping is very popular after purging of VSCs from different waters and therefore will be also discussed in Section 3.1.2.2.

Ivey and Swan [71] compared the automated GC system, based on cryotrapping of DMS and CS_2, with a gold-coated glass wool trapping with atomic emission detector. The comparison was considered acceptable, as the results were within a single population variation.

Cryogenic traps are usually installed outside the GC oven as they are relatively large and of high heat capacity in condensation and thermal desorption processes. These disadvantages can be overcome by cooling the first segment of an analytical column or a precolumn installed in front of it. Kono and Kuwata [112] described a small, light and low heat capacity cold trap easily installed inside any GC oven. The trap can be cooled to any desired temperature down to −165°C by differentially controlling the flow-rate of liquid nitrogen to the cold trap. Recently, a laboratory-made cryotrap that can be mounted on top of any GC oven in front of a GC column was constructed and optimised [111,140]. As the cryogens, either suspension of solid CO_2 in compressed air or vapours of liquid nitrogen could be applied.

3.1.2. Sampling from liquid matrices

Aqueous samples for the analysis of VSCs are usually collected into different glass or polymeric bottles [56,87,90,91,102,107,113,114]. Vessels, the first type are frequently silanized in order to minimize losses of sulphur compounds due to possible adsorption on the walls. Usually they are dark to stop biological and chemical processes which can occur under the influence of light. Teflon and polyethylene are used most frequently for polymeric bottles. During sampling, the vessels should be filled to the top to minimize air entrance and minimize head space and therefore minimize partitioning into the gas phase.

Because direct analysis is usually impossible, different preconcentration or isolation procedures are applied before the analysis proper. Two gas extraction techniques, i.e., static (head space – HS) and dynamic (purge and trap – PT) gas extraction techniques are most popular.

3.1.2.1. Liquid extraction

The solvent extraction technique is not frequently applied because this technique has several disadvantages, i.e., handling toxic solvents, the trapped substances become diluted, automation is difficult and the procedures are time consuming. The most popular solvents for the VSCs were: diethyl ether, hexane or mixtures of these solvents [115–117].

3.1.2.2. Gas extraction techniques

(1) *Static methods*. The static head space (HS) technique is especially useful for the determination of trace concentrations of volatile substances in samples that are difficult to analyse by conventional chromatographic means. In combination with gas chromatography (HS–GC) it allows the determination indirectly of volatile components in liquid or solid matrices by analysis of the vapour phase that is in thermodynamic equilibrium with the sample in a closed system. This technique is recommended for dilute solutions where the matrix can obscure the component of interest, damage a column or require extensive sample clean-up prior to the analysis.

HS–GC analysis was applied successfully for the analysis of VSCs in different matrices [118–123]. It also found application in physical chemistry of these compounds, being a valuable tool for acquiring data on gas–solid and gas–liquid systems. For example, it was used for the determination of distribution coefficients, *K*, of selected organosulphur compounds in air–water system as well as their temperature, ionic-strength and concentration dependencies [120]. HS–GC also found application in the analysis of VSCs in different matrices. Using this technique DMS was determined in blood and adipose tissue [121]. Blood (0.2 ml) and adipose tissue (0.5 g) with added DMS were sealed in a 10-ml vial using PTFE sheet to prevent escape of dimethyl sulphide from the head space. Equilibrium was achieved at 60°C

for 4 h, and 20 μl of gaseous phase was subjected to GC. Deruaz et al. [22] using commercial headspace device used this technique to identify 15 labile and unstable sulphur compounds in garlic. Keeping the device at 70°C they compared two time intervals (5 and 45 min) for sample heating. HS–GC was also successfully used for the determination of VSCs in water–alcohol solutions and brandies [122]. The authors found that headspace concentration of sulphur species H_2S, MeSH, EtSH, DMS, CS_2, DES, thiophene, DMDS and DEDS in the investigated solutions rises with increasing ratio between the gas and liquid phase volumes and was proportional to the temperature. However, it diminished with increasing ethanol content and was barely sensitive to the liquid-phase salt concentration. Ramstad et al. [123] analyzed hydrogen disulphide in a pharmaceutical formulation (pioglitazone). H_2S was measured in headspace over an aqueous granulated pioglitazone–citric acid (1:1) mixture.

(2) *Dynamic methods*. Among many dynamic gas extraction techniques, one technique, i.e., PT found the most extensive application in the preconcentration of volatile constituents from liquid matrices [124]. In the first step of the PT method, analytes are stripped from the aqueous phase. In the next, the swept compounds can be either: (1) adsorbed on a thermally desorbable sorbent bed (especially earlier mentioned Tenax) or (2) retained in a cold trap (cryotrapping), (3) cryofocused on the head of the column or transferred to a capillary column maintained at a cryogenic temperature (whole-column cryotrapping).

Different commercial and laboratory-made purge and trap assemblies were used for isolation and preconcentration of volatile sulphur species in different waters [7,14,34,65,87,88,90,101,102,105,107–109,114,125–131]. Because the extraction efficiency varies with the gas considered and the extraction facilities employed such as the dimensions of the purge vessel, bubble size distribution, sample volume and temperature, purge gas flow-rate and sparge time, all these parameters should be carefully considered before applying for a particular purpose. The PT system always contains a purging vessel with capacity ranging from 10 cm^3 to 2 dm^3. The purge gas can be delivered from a separate line or as a GC carrier gas to the vessel through a tube ended with a glass frit to maximally expand the contact surface between the liquid phase and gas which passes through a solution and transports the analytes. During purging, the solution sometimes can be stirred and heated. The following gases were used for stripping the VSCs from aqueous samples: nitrogen, helium, hydrogen and compressed air. In order to avoid any interference problem it is important to use precleaned gases. A typical flow-rate ranged from 20 to 50 cm^3/min but in some cases higher flows, such as 60–200 cm^3/min were applied. Because stripping efficiency is one of the critical points of the whole procedure many authors undertook the studies on the recovery of the investigated sulphur compounds. If sorbents are used in the second step of the procedure the breakthrough volumes of adsorbent should be taken into consideration. In the case of cryotrapping, the temperature should be sufficiently low to ensure quantitative trapping of the most volatile compounds.

Due to the low detection limits which can be obtained with the PT technique it was extensively used to determine some VSCs in different waters [14, 90, 91, 102, 104, 105, 107, 108, 129, 130,132,133]. Several PT procedures were elaborated especially for the most important natural sulphur compound – DMS [14,108,129,130]. This technique was also applied for the determination of sulphur species in sediments [88,107]. The suitability of another dynamic gas extraction technique, the thin-layer headspace technique utilizing a countercurrent flow of gas (abbreviated as TLHS), to isolate sulphur compounds from water has been also proved [134].

3.1.3. Removing of water from the gas streams

The main disadvantage of the PT technique is the purging of significant amounts of water vapour with the analytes. Water is also present in gaseous samples. This ubiquitous presence of water can cause many problems, mainly during the focusing of the analytes and their chromatographic analysis. The same problem is encountered during determination of VOCs in air samples, but the content of water is considerably lower. The main problems caused by the presence of water in streams of gases in the PT procedures and in air samples are as follows: decrease of the adsorption capacity of the sorbent used for the concentration of VSCs owing to co-adsorption of water; condensation of water along with the

analytes on the walls of the tubes connecting the purge device with the sorbent traps and GC injection port; plugging of traps and GC columns at sub-zero temperatures; degradation of the performance of retention gaps or GC columns; and variations of retention times and responses of the sulphur compounds that elute near water.

Several procedures have been used to avoid these adverse effects in the analysis of VSCs. The use of different desiccants was very popular for the water removal. Tangerman [89] recommended $CaCl_2$ as a drying agent for pretrapping water during the determination of VSCs in air. The drying agent placed in a small glass tube which was installed in the sampling line between Tenax trap and the sampling device, was used to prevent build up of water in the Tenax trap tube. Potassium carbonate was also tried as a drying agent [63,87,101,102,105] and found that recovery of DMS decreased by a factor of 3 [102]. Similar results were obtained for CS_2 and DMS. In addition, H_2S and MeSH were both totally adsorbed in the K_2CO_3 drying devices. Sulphur dioxide, being acidic is lost due to its reaction with potassium carbonate.

More frequently, a permeation removal of water by using membrane tubes was applied [48,62,70,105,107,109,129,135–139]. A commercially available Nafion drier (perfluorosulphonic acid membranes) immersed in a molecular sieve 5A has proved to be an efficient membrane separator in the analysis of sulphur species [139]. The losses of thiophene, DMS and propanethiol at the ppb level were less than 5%. Ridgeway [130] dried a purge gas to a dew point of about −70°C using a Nafion drier followed by a dry ice trap after purging DMS from seawater. To prevent clogging of the cold trap during determination of DMS, CS_2 and DMDS in surface seawater Tanzer and Heuman [105] installed a glass tube filled with potassium carbonate or a Nafion drying tube in front of it. Both drying tubes effectively removed moisture from the carrier gas stream without affecting the compounds of interest.

3.1.4. Sample storage stability

In order to avoid losses or possible transformations of sampled sulphur compounds samples should be analysed as soon as possible.

Lau examined the whole-air sampling with Tedlar bags [59]. The sample stability study was conducted by preparing a known ppb concentration mixture of the six sulphur gases (SO_2, H_2S, COS, CS_2, MeSH and EtSH) and storing it in a 5 dm^3 Tedlar air sampling bag. The concentrations were followed every 20 min for the first 3 h, and then periodically for the following 21 days. The obtained results were encouraging. Although Tedlar bags were not suitable for SO_2 and H_2S (SO_2 concentration decreased from 22 ppb to less than 1 ppb in 2 h and H_2S lost half of its original concentration of 70 ppb in about 10 days), the stability of other sulphur gases in the bags was good for two weeks even at the ppb concentration.

Changes of 5 reduced sulphur species (H_2S, COS, MeSH, DMS and CS_2) collected in glass sampling bulbs were determined as influenced by gas matrix (nitrogen, dry and moist air) and moisture [57]. The results have shown that reduced sulphur gases collected in glass bulbs can remain in the bulbs for approximately 24 h without major changes in gas concentrations if the sample is dry and does not contain oxygen (concentration decreased less than 5%). Dried air samples should be analyzed within 3 h. Glass bulbs are not useful for collecting sulphur gases if the sample in the bulbs contains moisture (significant decrease in H_2S and MeSH concentrations was observed).

Keeping the samples in subambient temperature can improve the stability of sulphur compounds. Reduced sulphur concentrations in an air sample collected cryogenically using Pyrex glass tubing trap and stored in a freezer were found not to change over a 2-week period [62]. Caron and Kramer [104] have found that in spite of storing samples of natural freshwaters only a few hours on ice in a cooler (0–4°C) and in dark until analysis, the replicate determinations gave a reproducibility of 5% for COS, MeSH, CS_2 and DMS, and 10% to 25% for DMDS. Moreover, the results varied with time of storage among subsamples. Relatively high standard deviation was attributed to microbial activity in the stored sample. To suppress microbial activity the authors have tried different phenols but the results were not conclusive.

The stability of 4 sulphur compounds (DMS, DES, propanethiol and thiophene) in aqueous solution (doubly distilled and purified water from Mili Q-Plus System) at a concentration of about 100 ppm each, kept in glass vials with silicone membranes was

determined as a function of temperature and storage time [111,140]. When the sample was kept in a refrigerator (ca. 4°C) the concentration decrease was considerably lower (less than 5% after 24 h) in comparison with storing at ambient temperature (about 20%). Holdway and Nriagu [129] have also found that the stability of freshwater samples was strongly affected by the temperature at which it was stored. They suggested that the stability of DMS in freshwater is shorter than the 48 h reported for seawater [14].

When immediate analysis is not possible refrigeration of samples for analysis of DMS in aqueous solutions was recommended as the best way to maintain sample integrity at least for periods up to 48 h [108]. As much as 50% of DMS was lost during several weeks storage and/or handling of the frozen (−20°C) sample of seawater for sequential analysis of DMS and dimethyl sulphoxide (DMSO). Because the presence of reduced sulphur compounds in seawater is closely related to biological activity, the stability of the sample may depend on the depth of sampling [100]. When a sample was taken from the Baltic Sea at 4-m depths and was stored at 5°C in the dark the concentration of DMS first rose dramatically after 4 days (nearly 10 times) and later decreased. Concentration of sample taken from 50 m depth did not change over a 2-week period. Samples can most probably be stored longer if the cold trap was maintained in liquid nitrogen. Tangerman [89] confirmed that Tenax trap containing VSCs collected from air could be stored for at least 1 week at −196°C in liquid nitrogen without any loss of sulphur compounds.

The samples containing high concentrations of H_2S (waters collected from the an oxic hypolimnium of one lake) should be preserved with excess of mercuric chloride in order to avoid interferences with determinations of other reduced sulphur compounds [87].

If possible, the determination should be made in the field immediately after sample collection to eliminate storage artefacts.

3.1.5. Silanization

Irreversible adsorption of the polar sulphur compounds on different surfaces of the analytical systems (both during sampling as well during proper analysis) is frequently responsible for losses of these compounds, especially when they are present in the low and sub-ppb range. Therefore, a surface-deactivated procedures of such surfaces are the most likely solution to such problem [141,142].

Different types of glass are most frequently used for sampling and isolation equipment (sampling bottles, reaction vials, purge flasks, sorption and cryogenic traps). The simplest way of deactivation of glass surfaces is a thorough cleaning and conditioning. Farwell and Gluck [141] cleaned the glassware by soaking in Chromerge at least for 15 min and rinsing with Millipore water followed by 1-h (minimum) soak in 10% HCl, rinsing and drying with acetone. More efficient are chemical deactivation procedures which can be categorized into four general types: (a) surface-active agents, (b) non-extractable films of polar compounds as Carbowax (20M or 1000), (c) silylation and (d) siloxane polymers. The third procedure was most frequently applied in deactivation of glassware in analysis of VSCs [62,87,100,102,105,107,108,127,141,142]. During silanization (silylation is synonymous term) reaction, the surface hydroxyl groups of a glass are replaced with silyl ether groups. Modifications produced in such manner are extremely stable owing to the strength of the Si–O–Si linkage. The polarity and chemical character of the modified layer that is formed by silylation can be controlled by the choice of constituents of the silylation reagent. The silylation is usually performed by immersing of glass equipment into 1–5% solution of appropriate deactivant. Four alkyl chlorosilanes were frequently used for this purpose: dimethyldichlorosilane (DMDS), hexamethyldisilazane (HMDS), methyltrichlorosilane (MTCS) and trimethylchlorosilane (TMCS). The solutions of these compounds are prepared in dichloromethane, hexane or toluene. Farwell and Gluck [141] compared degrees of Pyrex glass surface passivation for over 25 chemical deactivants and their related pretreatment procedures. Silanization of a chromatographic column is usually conducted by passing the vapours of single or mixture of silyl reagents (e.g. HMDS and TMCS) through the column for certain time (e.g., 30 min) [144].

3.2. Chromatographic analysis

Due to its unexcelled separation capability and facile compound determination gas chromatography

(GC) is still the most frequently used as a technique of the final determination of VSCs in different matrices. The analysis of low levels of sulphur containing compounds is complicated by two factors:
– The sorption and loss of sulphur species in the chromatographic system, and
– Problems with sensitive and selective detection of these compounds in complex matrices. Additionally, sulphur species having different physico–chemical characteristics need very effective separation systems.

3.2.1. Direct analysis

Direct chromatographic analysis of VSCs is favoured because it can reduce the analysis time by eliminating time-consuming procedures of samples preparation, which can additionally cause contamination or loss of analytes. Such procedures are possible when concentration of the sulphur species is higher than detection limits of chromatographic detectors. Therefore, there is continuous need for development of new sulphur-sensitive detectors. Interference problems may be sometimes omitted by using highly efficient separation systems. Direct procedures are especially needed during research expeditions, directly aboard ships or in situ for real-time measurements.

3.2.2. Chromatographic columns

Column packing for chromatographic determination should be chosen not only with respect to the complete separation of a given mixture but also column material and packing should be selected with respect to diminish losses due to adsorption and catalytic reactions and rearrangements. This is particularly important when packed metal and glass column are used.

The most common material used for packed columns in analysis of VSCs is PTFE [8, 23, 40, 57, 59, 62, 87, 91, 99, 102,104,107,108,111, 113,118,138,144–147]. The following packings were the most frequently applied in analysis of sulphur species:
– Supelpack S (specially treated Porapack QS) [144,148],
– different Chromosorbs [118,145,149],
– Porapack Q, N or QS [18,87,114,150–152],
– Triton X—305 [153,154]
– Chromosil 310 or 330 (specially treated silica gel) [8,23,59,62,99,102,110],
– Carbopack B or BHT 100 [40,91,107,108,138, 146,155]
– 3% Polyphenyl ether and 1% phosphoric acid on Chromosorb T [147].

Development of fused-silica capillary columns has provided more neutral material facilitating trace sulphur analysis. Broad application in the analysis of VSCs found especially methyl silicone phases (like BD-1 or Rtx-1) [22,24,71,76,109,111,116,122,143, 156,157] with thick films (4–5 μm). As with most analysis, no single capillary column can assure the combination of sample capacity, good resolution and reasonable analysis time for the wide range of sulphur species in different sample matrices. The effect of a stationary film thickness of methyl silicone phases, column length and internal diameter for the determination of sulphur compounds in hydrocarbon matrices has been evaluated by Hutte et al. [156]. Columns with thicker films (4 and 5 μm) provided increased separation of volatile sulphur compounds and were better suited for analysis of low level volatile sulphur compounds in gases.

Recently, porous-layer open tubular (PLOT) columns with Poraplots deposited on the column become commercially available. The usefulness of such columns was demonstrated for analysis of sulphur compounds such as COS, H_2S and DMS [71,92,123,158].

Representative examples of packed and open tubular columns with chromatographic conditions for analysis of sulphur compounds in different matrices are presented in Tables 3 and 4, respectively.

3.2.3. Detection systems

An attractive feature of a GC method is the availability of a large number of sensitive, universal and selective detectors. The latter detectors are especially useful in the analysis of different contaminants in increasingly complex matrices. Such detectors can reduce the analysis time by eliminating laborious and time-consuming procedures of sample preparation, which can also often cause contamination or loss of analytes. Due to these reasons selective detectors found extensive application in determination of environmental sulphur compounds. A survey of currently available sulphur-sensitive

Table 3
Examples of packed columns used for analysis of VSCs

Sample	Column material and dimension	Packing	Temperature conditions	Detector	Reference
H_2S, COS, DMS, CS_2, MeSH	PTFE, 2 m×3.15 mm I.D.	Carbopack B/ XE 60/H_3PO_4	2 min at −15°C, −15–85°C at 25°C/min	FPD	[138]
CS_2, DMS, DMDS, MeSH	PTFE, 3.2 m×3.2 mm O.D.	Chromosil 330	2 min at 30°C, 30–41°C at 5°C/min, 1 min, 41–100°C at 30°C/min, 100°C at 8 min	FPD	[75]
H_2S, COS, SO_2	PTFE, 46 cm×3.2 mm I.D.	Supelpack S	12 min at 70°C, 70–140°C at 35°C/min, 140°C at 1 min	FPD	[145]
C_1–C_4 thiols	Glass	15% SF96+6% OV225 on Chromosorb W	65°C	PID	[78]
COS, CS_2, MeSH, EtSH, SO_2	PTFE, 2 m×3.2 mm O.D.	Chromosil 310	1 min at 30°C, 30–95°C at 20°C/min, 95°C at 7 min	FPD	[76]
H_2S, COS, DMS, MeSH	PTFE, 1.4 m×3.2 mm O.D.	Carbopack BHT	75°C	FPD	[74]
DMS	PTFE, 3 m×3.18 mm O.D.	3% polyphenyl ether and 1% H_3PO_4 on Chromosorb P	30–60°C	MS	[150]
H_2S, COS, SO_2, DMS, DMDS, MeSH, EtSH	PTFE, 0.5 m×0.25 mm I.D.	Porapak QS	3 min at 40°C, 40–150°C at 7°C/min	FPD	[104]
H_2S, COS, DMS, CS_2, DMDS	Glass, 3 m×2.6 mm I.D.	25% oxydipropionitrile	1.9 min at 35°C, 35–80°C at 30°C/min, 80°C at 2 min	FPD	[161]
DMS	Glass, 3 m×2.6 mm I.D.	10% polyphenyl ether OS 124	60°C	FPD	[121]

detectors has been published recently [159]. Table 5 lists the basic characteristics of the most frequently used sulphur-sensitive detectors in the analysis of sulphur species.

Flame photometric detection (FPD) is still the most widely used sulphur-selective detection method in analysis of VSCs in environmental samples [8,14,23,40,57,59,62,87,93,94,100,102,107–109,111, 112,114,121,138,143,144,160]. FPD exhibits a non-linear (exponential) response to sulphur compounds and compound-dependent response factors, but is relatively inexpensive, robust and adequate for many applications. An attractive alternative to FPD is sulphur chemiluminescence detection (SCD). Latest applications of this detection methods have shown that SCD proves good performance in terms of delectability, selectivity, linearity, and a uniform sulphur responses [71,122,156,157,161,162]. It produces a linear and nearly equimolar response to sulphur. These advantages cause that SCD is highly recommended for analysis of extremely complex matrices. A comparison of SCD and FPD for HRGC determination of atmospheric sulphur gases was recently published [157]. The low detection limit, fewer problems with interferences and noise stability allow SCD more flexibility in capillary column selection. The combination of fused-silica capillary columns and SCD provides a powerful tool for the measurements of trace levels of sulphur-containing compounds in complex matrices [156].

In the last few years, atomic emission detection (AED) was found to have a good combination of specificity and sensitivity for analysis of volatile sulphur-containing compounds [22,76,163,164].

Table 4
Examples of capillary columns used for analysis of VSCs

Sample	Column material and dimension	Packing	Temperature conditions	Detector	Reference
DMS, DMDS in presence of VOCs	Fused-silica 10 m×0.32 mm I.D.	Poraplot Q	7 min at 55°C, 55−210°C at 12°C/min	MS	[92]
MeSH, DES, DMDS, DEDS, thiophene, CS_2, ethylmethyl sulphide	Fused-silica 30m×0.32 mm I.D.	Polydimethylpolysiloxane (SPB-1), 4 μm	1 min at 35°C, 35–55°C at 10°C/min, 55–250°C at 25°C/min	SCD	[122]
DMS, DMDS, CS_2, MeSH	Fused-silica 50 m×0.32 mm I.D.	SE-54, 5μm	3 min at 70°C, 70–180°C at 3°C/min	FPD, AED, ECD	[105]
DMS and higher sulphides (up to C_6)	Fused-silica 25 m×0.31 mm I.D.	Diphenylpolysiloxane (5%)+dimethylpolysiloxane (95%), 0.53 μm	2°C at 40°C, 40–70°C at 30°C/min, 70–205°C at, 7.5°C/min, 205–250°C at, 25°C/min	AED	[22]
DMS, CS_2, PrSH, thiophene, DES	Fused-silica 30m×0.32 mm I.D.	Dimethylpolysiloxane (Rtx-1), 4μm	2 min at 35°C, 35–70°C at 4.5°C/min, 70°C at 2 min	FPD	[109,111]
CS_2, DMS, DES, DMDS, C_1–C_5 thiols	50 m×0.32 mm I.D.	Polymethylsiloxane, 1 μm	20–100°C at 4°C/min	FPD	[24]
Different VSCs	25 m×0.25 mm I.D.	Cross methylsilicone	1 min at 50°C, 50–280°C at 8°C/min	MS	[116]
VSCs and VOCs	50 m×0.22 mm I.D.	OV-1701, 0.5 μm	10 min at 10°C, 10–300°C at 6°C/min, 300°C at 10 min	MS	[88]
COS, H_2S, DMS, MeSH	25 m or 50 m	UCON 50 HB 5100	0–45°C at 3°C/min	FPD, MS	[90]
H_2S	27 m×0.32 mm I.D.	Poraplot U	110°C	ELCD	[123]

Table 5
Basic characteristics of gas chromatographic sulphur-sensitive detectors [159]

Detector	Detection limit (gS/s)	Selectivity	Linear concentration range (decades)	CC coupling[a]	SFC coupling[a]	Ease of operation[b]
FPD	10^{-11}	10^{-3}–10^{6}	3	+	+	2
ECD	variable up to 10^{-15}	variable	4	+	+	1
SCD	10^{-13}	10^{6}–10^{7}	3–4	+	+	1
AED	10^{-12}	10^{4}	3–4	+	+	3
HECD	10^{-11}	10^{4}–10^{6}	3–5	+/−	−	4
PID	10^{-12}	poor	6	+	−	2
MS	10^{-11}	specific	5	+	+	4
FTIR	10^{-10}	specific	4	+	+	4

[a] Capability to couple with (CC=capillary columns, SFC=supercritical fluid chromatography), +=yes; −=no.
[b] 1=simple; 2=moderate; 3=difficult; 4=complicated.

AED can be used to confirm the elemental composition of a compound by its ability to monitor many atomic lines simultaneously. The response of AED to sulphur at 180.7 nm is reported to have linear range of 20 000, and sensitivity of 1.7 pg S/s and a selectivity over carbon of 15 000 [165]. The application of AED for the quantitative analysis of some sulphur species in different matrices has recently been described [76,163,164]. Also, a comparison of SCD and AED has been documented [166].

Electrolytic conductivity detection (HECD or Hall detector) has not found too many applications in analysis of VSCs probably because its usage requires regular attention [102,116,121,167]. The electrolyte must be kept extremely clean and its sulphur specificity is limited by high concentrations of co-trapped carbon dioxide. But despite these problems, HECD performed well in the sulphur detection mode. The detector response was linear up to 50 ng tested sulphur, selectivity of sulphur to carbon was typically better than 10 000, and the limit of detection was 1 pg S/s [168].

The combination of GC with the independent spectroscopic techniques, mainly mass spectrometry (MS) have made the combined techniques extremely versatile sources of qualitative and quantitative information on variety of environmental samples. The application of the MS or GC–MS systems is still becoming more popular [88,90,92,116,146,147, 158,169–171] in the analysis of environmental sulphur compounds. Třiska et al. [169] determining sulphur compounds in underground reservoirs of natural gas and town gas (RSH, RSR and RSSR type compounds) by GC–MS were using the ion $CH_2{=}S^+H$ with m/z 47. The ion with m/z 45 was more intensive in some sulphur compounds, but was often found in oxygen compounds ($C_2^+H_4OH$) as well. Headley [116] detected 21 organosulphur compounds in water, industrial effluent, sediment and fish samples using automated GC–MS system. The sulphur compounds (DMS and DMDS among others) were detected in the approximate concentration range 0.1 to 2000 ppb. A GC–MS method for DMS and SO_2 determination in air in real-time at the sub-ppt level applying a high pressure selected-ion chemical ionization flow reactor has been developed [130]. The use of isotope dilution GC–MS for DMS determination in sea water provided relatively good precision better than 2%. Perdeuterated DMS ($[^2H_6]$DMS) was chosen as an internal standard to improve precision and to differentiate between aqueous and sampling-generated DMS. Analytes losses occurring during sample collection and storage, and fluctuation in detector sensitivity did not influenced the relative signal obtained for the isotopomers. In that case by using the ratio of the MS response at m/z 62 and m/z 68, compensation was made for instrumental drift as well any losses in sampling ambient air. Another significant advantage was the ability to determine DMS concentration by stripping only a small fraction of DMS from solution, resulting in artefact-free DMS concentration. In addition, larger volumes of water could be sampled by eliminating the need for long sampling periods required to remove DMS quantitatively from solution. Kelly and Kenny [171] has demonstrated highly sensitive and specific continuous measurement of DMS in air using triple quadrupole mass spectrometry with atmospheric pressure chemical ionization. Detection limits in continuous direct monitoring were determined for DMS (2–4 pptv), H_2S (1 ppbv), for MeSH, COS and CS_2 (about 10 ppbv). Quite recently an interesting method using a modern rapid membrane inlet mass spectrometric technique (MIMS) in analysis of sulphur compounds in water was proposed [119]. The analysis with MIMS involved flowing the sample over a sheet of polysilicone membrane which extracted relatively non-polar and low-molecular-weight organic compounds from the matrix. The extracted organics pervapourated through the membrane into the ion source of MS, and the analysis was performed in a few minutes. The sensitivity of the MIMS method was comparable with that of the GC–FID method.

3.2.4. Calibration

The preparation of reliable standard mixtures is important step of each analysis. The simplest way of the calibration of a GC system in case of gas analysis is injecting a suitable volume of a standard gas into a separation column. Low-concentration standards, usually needed in trace analysis, are obtained by applying the exponential dilution flask technique

[172]. The step is repeated a number of times with varying concentrations and a calibration graph is drawn. To minimise nonlinear response problems (as for flame photometric detector) the calibration curves should cover the range of an ambient samples. Several compressed commercially available sulphur gas standards (DMS, H_2S, COS, MeSH and CS_2) were used in analysis of VSCs [93,100,144,160,171]. More frequently, the commercial or laboratory-made permeation devices were applied [14,34,59,62,70, 76,91,104,107,114,118,138,146,173]. Permeation rates (usually in range of ng S/min) are measured gravimetrically at suitable intervals of time (e.g., every second week). The permeation tubes are continuously flushed with suitable gas (usually nitrogen) in a vessel held in a water bath at desired temperature (e.g., 30°C). For calibration the gases from diffusion tubes are diluted with gas and frequently led through a glass loop injected onto the column with appropriate valves. A new concept for generation of standard mixture of thiols based on thermal decomposition of a substance chemically bonded to the surface of silica gel has been developed [174–176]. The method enables preparation of a standard mixture containing volatile, malodorous, unstable and toxic compounds. For example, standard mixture of MeSH and PrSH were generated by heating silica gel with anchored dithiocarbamate groups [174,176].

In analysis of liquids, primary standards are usually prepared in appropriate solvent in which standards are well soluble. When nonselective sulphur detectors are used, the solvent should not interfere with determined compounds. But for sulphur selective detectors so called quenching effects may take place. Sulphur standards are made of analytical grade liquids most frequently by dissolution in hexane [87], benzene [65], diethyl ether [90,121], dichloroethane [94], methanol [61,87, 107,111,134] or ethanol (to reduce losses by volatilisation) [87,122] and in degassed ethylene glycol [97,105,129,130] or dimethyl sulphoxide [120]. Working standards are prepare by adding a suitable amount of primary standards to aqueous solutions. All standard solutions should be stored in vials with head space volume as small as possible and be stored at a lowered temperature.

4. General scheme of volatile sulphur compounds determination

The presented problems with the determination of environmental sulphur compounds show the complexicity and broadness of this type of analysis. To facilitate the orientation of the reader in this field, the scheme of typical procedures employed in the trace analysis of volatile sulphur compounds in gaseous and aqueous matrices, is presented (see Fig. 1). Rarely used procedures (e.g. direct analysis) and steps not always required (e.g. band focusing) are indicated by dashed line.

5. Conclusions

The review attempted to present the examples of problems encountered in the analysis of volatile sulphur compounds in environmental samples by means of a gas chromatography. It can be said that most qualitative and quantitative analysis of VSCs in environmental matrices can be performed only by a combination of efficient sample enrichment, quantitative desorption from different traps, high resolution separation of sample components, minimal adsorption losses to the analytical system and the specific detection of sulphur present in a compound. The significant progress was observed in many steps of VSCs analysis. But such procedures are not routinely used in many laboratories. The main reasons are the expensive equipment and time-consuming procedures. The future development should be focused on the procedures that can be used during long research expeditions, directly aboard ships, or in situ for real-time measurements.

6. Abbreviations

AED	Atomic emission detection
BTV	Breakthrough volume
DMS	Dimethyl sulphide
DMDS	Dimethyl disulphide
DEDS	Diethyl disulphide
DES	Diethyl sulphide
ECD	Electron-capture detection

HECD	Electrolytic conductivity detection
EtSH	Ethanethiol
FID	Flame ionization detection
FPD	Flame photometric detection
FT-IR	Fourier transform infrared detection
MS	Mass spectrometry
MeSH	Methanethiol
PID	Photoionization detection
PrSH	Propanethiol
PTV	Programmed temperature vapourization injector
RSC	Reduced sulphur compounds
SFC	Supercritical fluid chromatography
SCD	Sulphur chemiluminescence detection
VOCs	Volatile organic compounds
VSCs	Volatile sulphur compounds

Acknowledgements

The author thanks Dr. B. Zygmunt and Professor J. Namieśnik for their contribution to this review and for valuable suggestions and comments on an early version of the manuscript. This paper was supported by a grant No. 011822 from the Polish Scientific Committee.

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