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The method for on-site determination of trace concentrations of methyl mercaptan and dimethyl sulfide in air using a mobile mass spectrometer with atmospheric pressure chemical ionization, combined with a fast enrichment/separation system

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ABSTRACT

A method for fast simultaneous on-site determination of methyl mercaptan and dimethyl sulfide in air was developed. The target compounds were actively collected on silica gel, followed by direct flash thermal desorption, fast separation on a short chromatographic column and detection by means of mass spectrometer with atmospheric pressure chemical ionization. During the sampling of ambient air, water vapor was removed with a Nafion selective membrane. A compact mass spectrometer prototype, which was designed earlier at Trofimuk Institute of Petroleum Geology and Geophysics, was used. The minimization of gas load of the atmospheric pressure ion source allowed reducing the power requirements and size of the vacuum system and increasing its ruggedness. The measurement cycle is about 3 min. Detection limits in a 0.6 L sample are 1 ppb for methyl mercaptan and 0.2 ppb for dimethyl sulfide.

1. Introduction

Reduced sulfur compounds (RSC) have a great impact on global atmospheric chemistry and play a significant role in the formation of atmospheric aerosols and, eventually, in the processes of global climate change. In this connection, intensive studies of the natural concentrations of dimethyl sulfide (Me_2S) in the atmosphere have been carried out. Me_2S is produced by marine phytoplankton and algae and represents one of the major sulfur cycle channels [1]. Emissions of methyl mercaptan (MeSH) from ocean waters are less well studied but Kettle and colleagues [2] carried out extensive measurements and found that the MeSH flux rate from the ocean to the atmosphere ranges from 0.1 to 1.0 relative to Me_2S flux, depending on the region. Thus, it is presumed that MeSH is the second significant source of biogenic sulfur emitted from the ocean to the troposphere and calls for further in-depth research.

The sources of RSC emissions are natural as well as anthropogenic. Normally their concentration is within the sub-ppb range. Yet even a small excess in this concentration in the air of a populated region (caused by emissions from waste disposal facilities or large-scale livestock farms) can become a problem, as RSC are malodorous compounds with an extremely low odor detection threshold [3]. MeSH and Me_2S are also emitted by craft pulp production. In some countries, RSC levels are regulated by the state. In the Russian Federation, for example, the permissible exposure limit of MeSH for general population is 0.006 mg/m^3 (about 3 ppb).

The problem of RSC trace detection is also important in natural gas preparation before its transportation. RSC are important components of the odor of beer. They are also indicators of some types of food [4].

Quantitative analysis of low concentrations of RSC in air is complicated by their high reactivity, including photo-oxidation, and adsorption on different surfaces, which complicates sample processing. For this reason, the development of proper field instrumentation for accurate on-site determination has become a pressing issue.

Analysis of trace RSC in air is performed primarily with the use of gas chromatography [5,6]. Toda and colleagues [7] have developed an automatic Me_2S and MeSH level measurement method based on single column trapping/separation and chemiluminescence detection (SCTS–CL). The portable instrument was tested near Lake Baikal in East

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Siberia, with the set-up assembled on board the research vessel and on a van [8]. An important peculiarity of SCTS–CL is the use of a short column packed with silica gel, which at first concentrates and subsequently performs separation of the analytes. This provides for easier management and a relatively short measurement cycle. The technique and instrument described allow for cyclic Me_2S and MeSH measurements to be taken at 15 min intervals.

The linear response of SCTS–CL for Me_2S and MeSH within the range of 1–21 ppb was validated as a result of an intercomparison between SCTS–CL, gas chromatography coupled with sulfur chemiluminescence detection and proton-transfer-reaction mass spectrometry [9]. The same study revealed that the high concentration of hydrogen sulfide in the air sample collected from a pig production facility interfered with the measurement, so its preliminary removal was recommended for reliable determination of MeSH.

Mass spectrometric determination provides better reliability and specificity of detection of chemical species, especially with complex matrices. Mass spectrometer miniaturization for the sake of its fieldability attracts many investigators [10]. At present, almost all portable miniature mass spectrometers use an electron impact ionization source. Although atmospheric pressure chemical ionization (APCI) mass spectrometry has proven to be an extremely sensitive technique for the selective detection of gas-phase species at low levels [11], this kind of apparatus is hard to miniaturize because of high gas load produced by the ion source, which requires a high capacity vacuum system. The first descriptions of APCI miniature instruments were presented by Makas [12] and Cooks [13] with colleagues. Following that, Cooks and Ouyang demonstrated the most impressive effort in this direction by developing the discontinuous atmospheric pressure interface [14] as the base for the most compact mass spectrometer with APCI to date [15]. The only disadvantage of this approach is its limited applicability for combining with fast chromatography system because of intermittent detection.

A special purpose mass spectrometer for underway shipboard analysis of Me_2S was developed [16]. The method involves APCI. Recorded ion is the $[(CH_3)_2S+H]^+$ adduct ion ($m/z=63$).We have found, and it will be discussed below, that this technique is not directly appropriate for MeSH detection because the ionization of MeSH requires specific conditions. Furthermore, the ionization of Me_2S leads to the formation of a fragment ion, whose mass coincides with the mass of a MeSH protonated molecule. This interference may become confusing in data interpretation when the two compounds are being registered simultaneously.

The purpose of the present study was to develop a technique for simultaneous detection of Me_2S and MeSH in air at 1 ppb, based on the mobile compact APCI mass spectrometric detector that we designed previously [12].

To eliminate cross-effect and to provide conditions for efficient ionization, we introduced the stage of chromatographic separation. In order to reach the required detection limits we implemented our previously designed direct flash desorption device for sample enrichment [17]. Efforts were made to minimize the gas load of the APCI ion source on the vacuum system. The purpose of these efforts was to miniaturize, ruggedize the system and to reduce its power consumption, which is critical for field equipment.

2. Experimental section

2.1. Mass spectrometer

The method developed is based on our previously designed APCI mobile compact mass spectrometer [12]. Its mass analyzer is

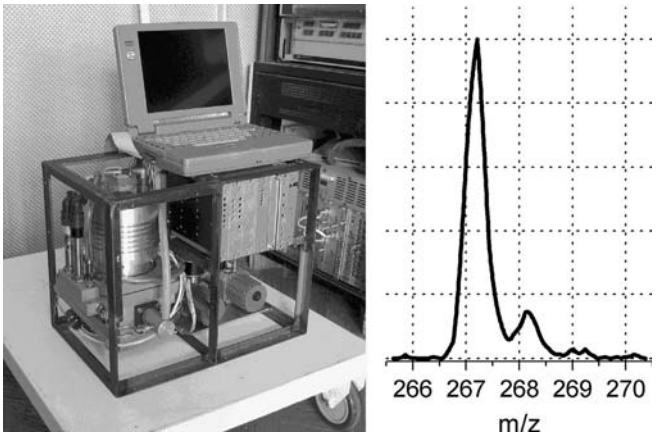

Fig. 1. The atmospheric pressure chemical ionization mass spectrometer for field detection. The fragment of tributyl phosphate mass spectrum, recorded at 10^{-3} Torr (0.13 Pa) in the mass analyzer region. The resolving power at 10% level $M/\Delta M=306$.

a 5 cm long monopole mass filter which retains resolution of at least 1M and sufficient transmission at a working pressure of up to 10^{-3} Torr (0.13 Pa). The operating frequency is 5 MHz. This device was successfully tested for the detection of organophosphorous compounds in air. We introduced a number of improvements into the configuration of the device (Fig. 1). The gas load of the ion source was reduced about threefold. The principal components remained the same, however. Primary ionization of air, which serves as carrier gas, is performed by a corona discharge in the positive mode. To transport ions from the ionization region at atmospheric pressure to the mass analyzer region, a two-stage differential pumping system is employed, as suggested by Kambara [18]. In our experiments the diameter of the ion source inlet aperture was 60 μm and its thickness—200 μm, which provided the input flow rate of 20 mL atm/min and pressure in the declustering region of about 2 Torr (267 Pa). The diameter of the aperture in the skimmer was 200 μm, providing an input flow rate into the mass analyzer region of about 2 mL atm/min. This configuration of the interface allowed the use of a small vacuum rotary vane pump with a pumping speed of 0.1 L/s (NVR-0.1D, Vakuummash, Kazan, Russia). The mass analyzer region was pumped down with a 100 L/s turbomolecular pump (NVT-100, Prizma, Iskitim, Russia).

The ion source temperature was 100 °C. The corona discharge current was 1 μA. The distance between the needle electrode and the inlet aperture was 1 mm. The distance between the inlet aperture and the skimmer was 2 mm. The energy of ions on entering the mass analyzer was specified by the skimmer's potential and amounted to 25 eV. Potential difference between the electrode with the inlet aperture and the skimmer, which determined the rate of collision-induced dissociation, ΔU, was kept within 0–200 V.

2.2. Enrichment/separation system

The schematic diagram of the method is shown in Fig. 2. In order to achieve 1 ppb level Me_2S and MeSH detection in air, preconcentration was necessary. To avoid cross-effect in the process of ionization, sample components had to be separated chromatographically. A large amount of moisture from air naturally becomes trapped by silica gel together with the analytes, which has an adverse effect on the analysis performance, since fast water desorption overloads the GC column. To eliminate this effect, most of the water vapor was removed by a PD-100T-12 MKS dryer with a multi-tube Nafion membrane (Perma Pure, USA)

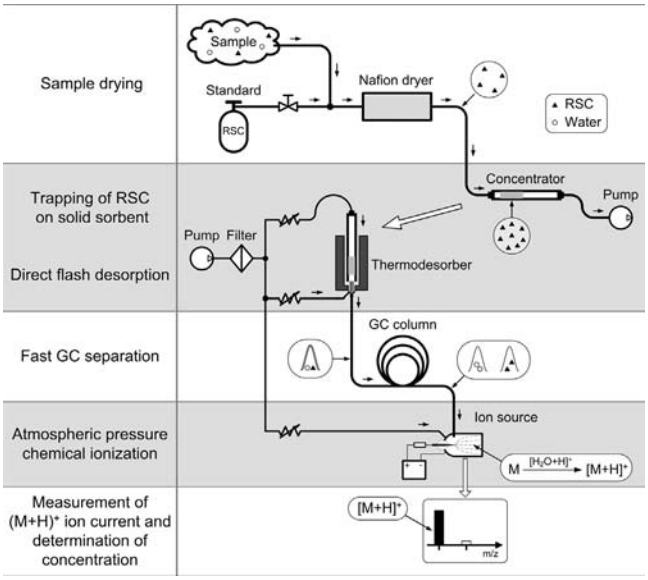

Fig. 2. Schematic diagram of the method of MeSH and Me_2S determination in air.

that reduced the sample's relative humidity to under 1%. According to the manufacturer's information, the Nafion membrane does not affect the RSC level in air.

The inlet system that we developed previously [17] involves direct flash thermal desorption. The concentrator comprised a thin-walled stainless steel capillary tube 2 mm in diameter and 120 mm in length, packed with a 10 mm long silica gel layer (KSMG, Karpov Chemical plant, Mendeleevsk, Russia) with particle sizes from 0.2 to 0.3 mm (adsorbent mass of approximately 10 mg). A custom-made automatic air sampler based on a diaphragm pump (Model 1410, Tomas, Germany) provided the sampling rate of 0.45 L/min. The flow rate of carrier gas through the concentrator during desorption was set equal to the rate through the GC column.

The GC short quartz capillary column (2 m, 0.32 mm, and 10 μm) PoraPLOT Q (Chrompack, Netherlands) inlet attached to the inlet system at atmospheric pressure. Its outlet was tightly connected to the ion source discharge region. The flow through the column was provided by underpressure at this region. Additional carrier gas flow was supplied to the discharge region through a needle valve. This valve regulated underpressure and determined the flow rate through the column. In our experiments, the flow through the column was restricted to 6.5 mL/min. Gas flow rates were measured by a ProFlow6000 flowmeter (Restek, USA). The separation was carried out in isothermal mode with the column temperature of 45 °C. Ambient air served as carrier gas. Its purification and dehydration to the dew point of under −55 °C were carried out with the aid of the filter purpose-built by Baldin and co-workers for portable chromatographic equipment [19]. Air humidity after dehydration was controlled by the IVG-1-KP hygrometer with an IPVT-08 sensor (ES&S, Moscow, Russia).

The result recording was carried out in the form of mass chromatograms by ions at $m/z=49$ and $m/z=63$ corresponding to the $[M+H]^+$ adduct ions of Me_2S and MeSH.

2.3. Calibration standards

To calibrate the method and to produce a standard concentration, reference permeation tubes were used: IM 38-M-A2 for MeSH and IM 75-O-A2 for Me_2S (Monitoring, Saint Petersburg, Russia). The emission rates of these tubes at 30 °C were 0.111 μg/min and 0.013 μg/min. A custom gas standard generator was assembled, which consisted of a thermostat with a temperature regulator, a carrier gas feed system and a two-step dynamic dilution system. The concentrations with single-step dilution employed at the 0.5 L/min flow rate were 112 ppb for MeSH and 10.4 ppb for Me_2S. In the case of two-step dilution, the concentrations ranged within 1.1–112 ppb for MeSH and 0.1–10.4 ppb for Me_2S.

3. Results and discussion

3.1. Features of methyl mercaptan and dimethyl sulfide ionization

Prior study of ionization of the analytes revealed several factors that set the requirements for the method in general and specified its analytical configuration. It was found that both an $[M+H]^+$ adduct ion and an M^+ molecular ion were formed, as well as fragment ions, in the positive mode of the corona discharge at atmospheric pressure (Fig. 3).

Presumably as a result of methyl cationization MeSH also produces an ion whose mass ($m/z=63$) equals the mass of the Me_2S protonated molecule. Me_2S gives two intense fragment ions of $m/z=47$ and $m/z=48$, which, due to sulfur isotopes ^{33}S and ^{34}S, produce a signal at $m/z=49$, the same mass as the MeSH protonated molecule. Peak ratios between parents and fragment ions depend on ΔU, whereas peaks that produce interference amount to 2–6%. Therefore, in the case of simultaneous detection of these two analytes, in order to avoid data misinterpretation, the analytes must undergo prior chromatographic separation. The most intensive ion for both analytes is an $[M+H]^+$ adduct ion; however, its formation is critically dependent on the humidity of carrier gas, especially in the case of MeSH (Fig. 4). This factor is responsible for the importance of prior removal of water vapor from the sample and carrier gas drying, as well as chromatographic separation of MeSH from residual water in the sample. The efficiency of dehydration is controlled throughout the monitoring of NO^+ precursor ion which forms in air in the corona discharge [20] because its abundance is inversely proportional to humidity (Fig. 4). Control of NO^+ peak intensity in chromatographic run also ensures that the sample is free from high concentrations of impurities, which inhibit analyte ionization.

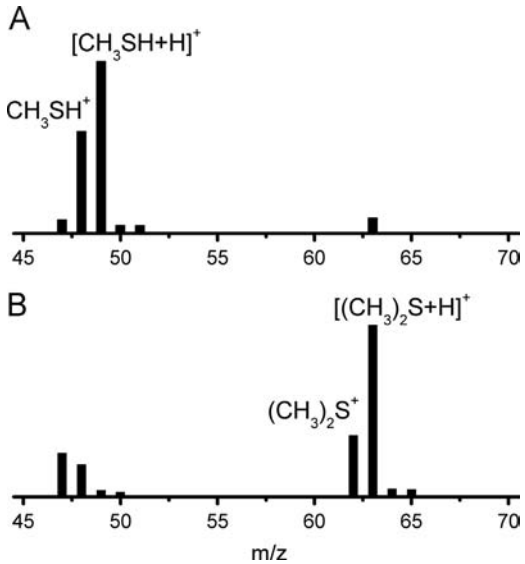

Fig. 3. Positive atmospheric pressure chemical ionization mass spectra: (A) MeSH and (B) Me_2S. $\Delta U=35$ V.

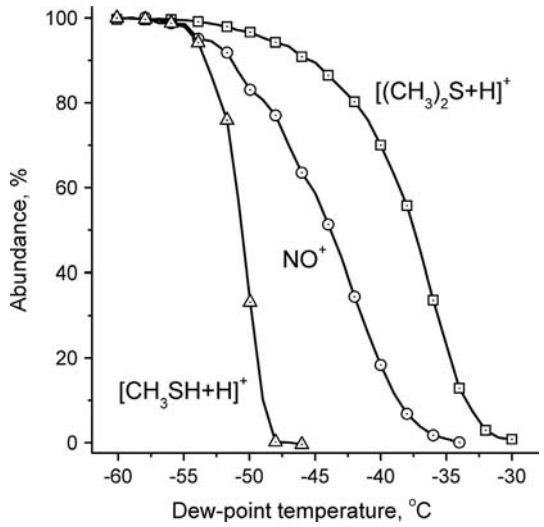

Fig. 4. The dependence of NO^+ reagent ion and MeSH and Me_2S $[M+H]^+$ adduct ions abundance on carrier gas humidity.

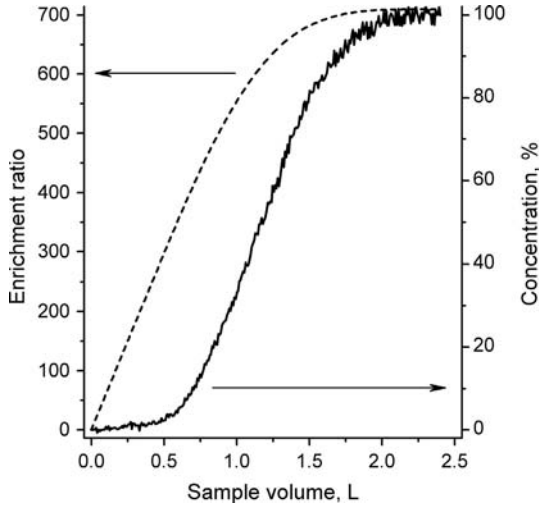

Fig. 5. The determination of breakthrough volume. Dependences of MeSH concentration on leaving the concentrator and of the calculated enrichment ratio on the sample volume.

3.2. Analyte enrichment in the inlet system with direct flash thermal desorption

The inlet system, described earlier [17], provides direct flash desorption of the sample by means of fast introduction of a low heat capacity concentrator into the massive preheated injector. The key feature of the inlet system employed in this method is that, thanks to the fast heating of the concentrator, volatile compounds of the sample become desorbed and fully transferred to the chromatographic column within about a second, which eliminates the need for extra focusing.

Earlier, this system, packed with Tenax adsorbent, had demonstrated good performance in the analysis of high-boiling volatile organic compounds at the desorption temperature of up to 350 °C. In the present study, Me_2S and MeSH sorption capacity was found insufficient, which necessitated the use of silica gel instead of Tenax. Me_2S and MeSH preconcentration was previously studied by Devai and colleagues [21], who obtained the best results using silica gel. Trapping and desorption property of silica gel for Me_2S and MeSH analysis has received an additional approval during mass spectrometric investigation [9].

Assuming that the analyte is fully trapped by the sorbent and that all trapped analyte is transferred to the column and then to the ion source, we have the following:

$$C_0\, V_{sample} \approx C_{in}\, Q_{in}\, \Delta t, \quad (1)$$

where C_0 is the analyte concentration in air, V_{sample} is the air sample volume, C_{in} is the analyte concentration in carrier gas in the ion source, Q_{in} is the inlet flow rate into the ion source, and Δt is the chromatographic peak width of the analyte in the ion source.

Enrichment ratio K is evaluated as the relation of the analyte concentration in carrier gas in the ion source (C_{in}) to the initial analyte concentration in air (C_0). Applying formula (1), we obtain the limiting enrichment ratio evaluation:

$$K = C_{in}/C_0 \approx V_{sample}/(Q_{in}\, \Delta t) \quad (2)$$

To work out the optimum sample volume, we investigated a breakthrough volume of the more volatile MeSH. Air mixture containing MeSH was supplied to the inlet of the concentrator whose outlet was directly connected to the ion source. The $[M+H]^+$ adduct ion was recorded. The obtained relation of signal intensity to the sample volume that specifies the breakthrough is shown in Fig. 5. Also shown here is the enrichment ratio, calculated by formula (2), with sample loss due to breakthrough taken into account. For a 0.6 L sample at air temperature 20 °C, less than 1.5% of the analyte is lost. For inlet flow rate $Q_{in}=20$ mL/min and MeSH chromatographic peak width $\Delta t=5$ s, the enrichment ratio is 360. Saturation of the concentrator is reached with the sample volume of about 2 L, in which case the enrichment ratio amounts to 700.

3.3. Chromatographic separation

Despite preliminary sample dehydration, insufficient separation led to the suppression of MeSH ionization by the residual water concentration in the 0.6 L sample. For this reason, the principal measure in the choice of chromatographic condition was the separation of MeSH peak from water peak. Water concentration controlled by the NO^+ ion ($m/z=30$). Similarly to MeSH, the NO^+ ion formation depends on water concentration. Fig. 6 demonstrates a typical mass chromatogram with retention time of 25 s for MeSH and 120 s for Me_2S. It is seen that the given separation is sufficient to resolve the MeSH peak from the water peak, because the latter coincides quantitatively with the NO^+ ion signal drop. Considering that the chromatographic run is performed isothermally, immediate introduction of the next sample is possible as soon as the last analyte leaves the column. Thus, the measurement cycle can be as short as 3 min.

It must be noted that the described conditions for chromatographic separation are not optimized for best sensitivity, because the dimensions of the column used in our experiments determine a high retention factor (over 20 for MeSH) as well as excessive linear speed of carrier gas and consequently result in considerable chromatographic peak broadening. We assume that optimizing these parameters and narrowing the peak would increase the analyte concentration by several times at peak maximum.

3.4. APCI mass spectrometer with low gas load

Reducing gas load allows for lower power requirements for the mass spectrometer's vacuum system, which determines the size and the weight of the whole system. It is common practice to use a fairly high gas flow of about 1 L/min in ion sources operating at atmospheric pressure, to ensure a greater ion yield from the

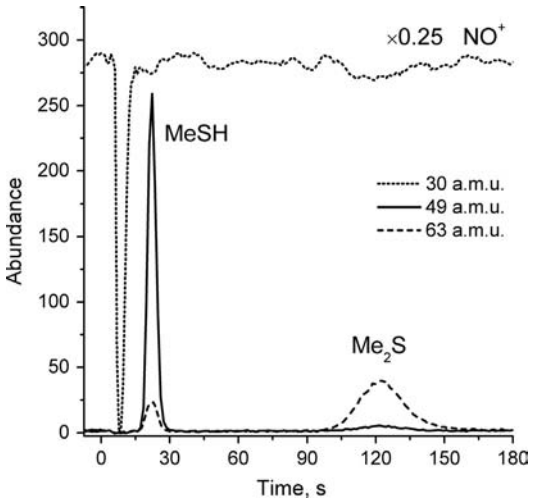

Fig. 6. The mass chromatogram of the $[M+H]^+$ adduct ions of MeSH ($m/z=49$) and Me_2S ($m/z=63$) and NO^+ reagent ion ($m/z=30$), resulting from the analysis of a standard mixture: MeSH at 56 ppb, Me_2S at 5.2 ppb.

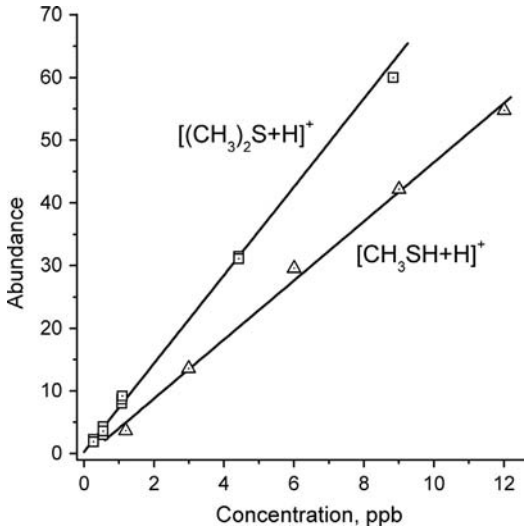

Fig. 7. Calibration curves for MeSH and Me_2S within 1–10 ppb range. Sample volume—0.6 L.

ionization region by means of their gas-dynamic transportation. On the other hand, a low input flow rate is preferable, when the sample is transferred into carrier gas entering to ionization region as a pulse, specifically as result of flash desorption or as chromatographic peak. In this case, lower carrier gas flow rate results in a higher concentration of analyte in the sample (see equation 2). Furthermore, narrowing the inlet aperture of ion source provides for better transmission through the declustering region of the apparatus because of lower ion beam divergence. By narrowing the inlet aperture we reduced inlet flow to 20 mL atm/min. The ion current passing through the inlet aperture was 1 nA. The total ion source output current passing through the skimmer with diameter 200 μm reached 0.35 nA, i.e. 35% of the current that entered the inlet orifice. The measured gas flow rate through the skimmer was 2 mL atm/min. The 100 L/s turbomolecular pump provides the pressure at the mass analyzer region of about 2.5×10^{-4} Torr (0.033 Pa). On the assumption that the mass analyzer operates within 10^{-3} Torr (0.13 Pa) pressure, the reserved pressure allowed us to either widen the aperture in the skimmer, thus increasing the ion output, or reduce the rate of the high-vacuum pump. In our case, the 25 L/s rate was sufficient. Considering the need for higher ruggedness of the system for mobile application in harsh environment, we reduced the rotation frequency of the turbomolecular pump from 510 cps to 280 cps, thus increasing the operational life of the pump, as well as its resistance to mechanical impact, such as tilting and rocking.

The total weight of the vacuum system components amounted to 10 kg and its power consumption was under 70 W. The weight of the whole system was about 25 kg. We expect to further reduce the weight of the system by implementing a more lightweight turbomolecular pump with 10 L/s pumping rate. This will require us to either limit gas load to 10 mL atm/min or reduce the skimmer capacity by about 2.5 times.

3.5. Performance of the method and its validation

Response intensity dependence on the analyte concentration in air was calibrated within the ranges of 1.1–112 ppb for MeSH and 0.1–10.4 ppb for Me_2S, and revealed linearity. The more important range of 1–10 ppb is represented in Fig. 7. Detection limits were evaluated as 1 ppb for MeSH and 0.2 ppb for Me_2S. At these concentrations, the signal-to-noise ratio was five.

In case of a series of measurements, in order to reduce the cycle duration, sampling can be performed while the preceding analysis is still in progress. The sampling time for a 0.6 L sample is 80 s. As soon as the system is ready for the analysis, the operator connects the concentrator to the line holding carrier gas and inserts the concentrator into the injector. The analyte desorption occurs within about 1 s. Normally, the concentrator stays in the injector for 10 more seconds for a complete drain-out before it can be withdrawn. The concentrator is then placed on a separate stand to cool down to the ambient temperature, which takes about 1 min. After that, it is ready for the next sampling. It must be noted that while using a set of several identical concentrators could facilitate the process, it is still preferable to use a single concentrator for a series of measurements in order to reduce inaccuracy. Considering that separation is performed isothermally, by the end of the chromatographic cycle (which takes about 3 min) the GC system and the concentrator with the new sample are ready for the next analysis. An example of measurement series is shown in Fig. 8. In this experiment a 1.5 L plastic tank with ambient air was filled with 140 mL of mixture generated by the standard concentration source, that contained 1700 ppb of MeSH and 160 ppb of Me_2S (resulting concentration 162 and 15 ppb respectively). The plastic tank had a concentrator connection port for sampling and an air inlet port for volume replacement. The stirring of gas in the tank was not performed. Thus, with sequential sampling the analyte concentration was decreasing approximately exponentially.

The method was tested at Lake Baikal in East Siberia, Russia, near the Baikalsk Pulp and Paper Plant. During the two-day expedition, the prototype was assembled on the research vessel *Vereshchagin* and cyclical air analysis was performed. Measurements were taken within three hours upwind from the plant. The MeSH level did not exceed 3 ppb. The maximum Me_2S level was 10.5 ppb.

The list of monitored compounds can be extended if necessary: this can be demonstrated by the analysis of beer headspace. Knowing a priori that acetaldehyde (a natural by-product of the fermentation process) was present in the sample and had a retention time close to MeSH, we used a longer (3 m) GC column in order to provide its proper separation from MeSH to avoid cross-effect in ionization. The sample was drawn directly from the bottle's neck. Since acetaldehyde concentration was considerably higher than RSC concentration, the former was recorded by $[M+H]^+ + H_2O$ water cluster minor peak ($m/z=63$), whose

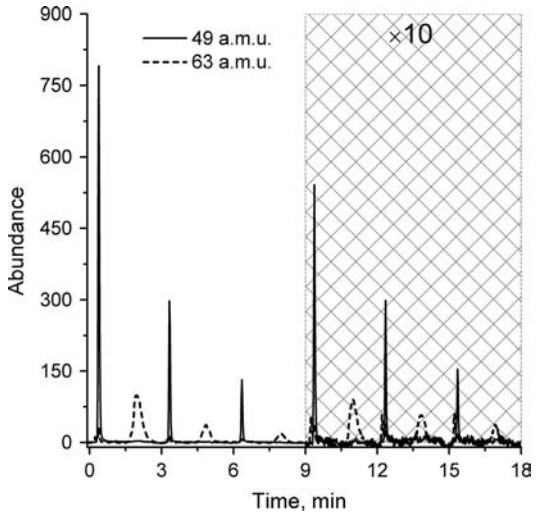

Fig. 8. The mass chromatogram resulting from the repetitive analysis of the mixture of MeSH and Me_2S with concentration changing as a result of exponential dilution. Signal at the crosshatched region is multiplied by factor of 10.

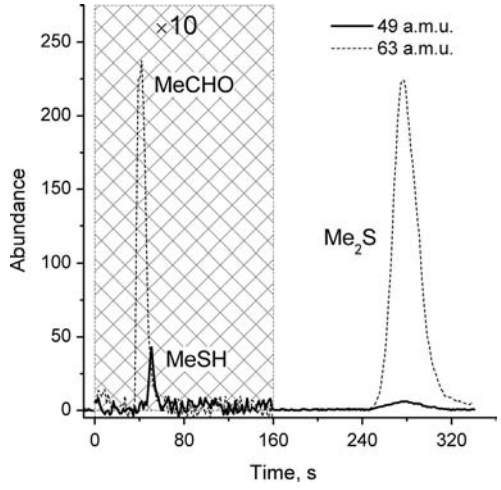

Fig. 9. The mass chromatogram resulting from the analysis of beer headspace. MeSH and Me_2S are represented by the $[M+H]^+$ adduct ions, $m/z=49$ and $m/z=63$ respectively, acetaldehyde is represented by the $[M+H]^+ + H_2O$ water cluster, $m/z=63$. Signal at the crosshatched region is multiplied by factor of 10.

intensity amounted to 0.7% of the $[M+H]^+$ adduct ion. The chromatogram is given in Fig. 9. As specified by the calibration, the MeSH and Me_2S concentration in beer headspace was 1ppb and 32 ppb, respectively.

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