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Cryogenic Trapping of Carbonyl Sulfide without Using Expendable Cryogens

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We report on a cryogenic trapping procedure that functions without the use of liquid cryogens at a trapping temperature of −150 °C. A heat-transfer device was designed that links a commercially available closed-cycle refrigerator to a cryotrap made of a glass-coated steel tube filled with Chromosorb W adsorbent material. This forms part of an analytical system incorporating GC separation with subsequent FPD detection, used for the analysis of carbonyl sulfide. The recovery is greater than 95% for trapping times up to 30 min. The analytical performance is excellent with both accuracy and precision better than 2%. Equipped with the new cryogenic trapping device, the measurement system is capable of continuous operation over a period of several weeks.

Cryogenic preconcentration of volatile analytes is a common procedure in many applications such as environmental science, food science, and industrial process analysis. Various designs for cryogenic traps have been invented and applied successfully.[1] Common to all cryogenic trapping techniques is that the analytes pass through a cooled section of an analytical system, where they stay until they are ejected in a relatively narrow band through the application of heat.

Moderate trapping temperatures down to about −60 °C can be achieved using relatively simple electronic devices or mixtures of ice and various salts.[2] Most trapping techniques for which lower temperatures are required make use of liquefied inert gases, such as argon and nitrogen. These liquids need to be replenished regularly, which makes their use expensive and impractical, especially for extended field use. A further consideration is the potential safety hazards involved with the handling and transfer of these liquids. Thus, a means of trapping analytes from air without using expendable cryogens is of great interest. A technique for cryotrapping atmospheric trace compounds inside the chromatographic column at −101 °C using a three-stage thermoelectric (Peltier) heat pump with a Freon refrigerator-cooled copper heat sink was previously described by Bertman et al.[3] According to the authors, the thermoelectric heat pump has the advantage that it can also be used as a heater to release the sample with a heating rate of ∼200 °C min⁻¹ and a power-limited
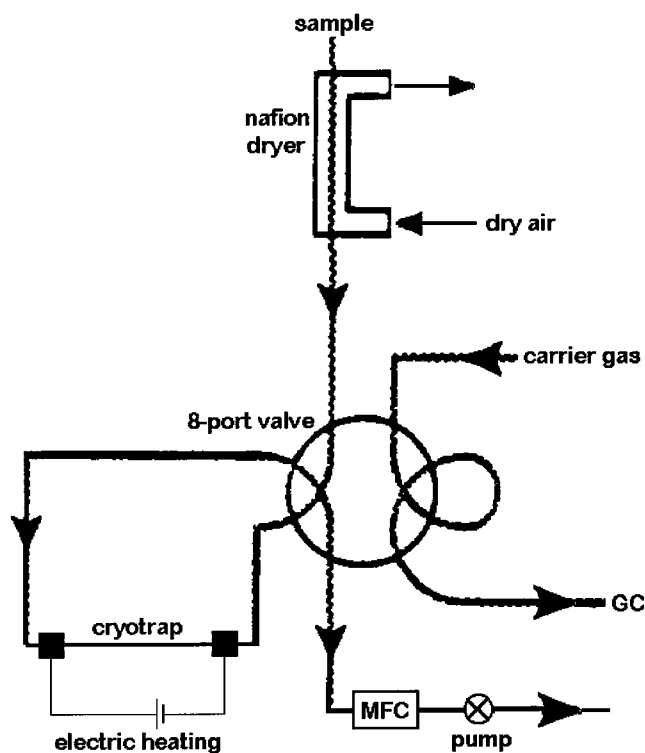

Figure 1. Automated cryotrap-GC−FPD sampling system.

maximum temperature of 35 °C. Application of an additional heat source is problematic because temperatures above 80 °C would damage the thermoelectrics.

An alternative method is described here that cools to −150 °C using only a commercially available closed-cycle refrigerator, interfaced to a steel trap that can be rapidly heated by applying an electric current. The system was used successfully for laboratory and field measurements of carbonyl sulfide at typical ambient concentrations.

EXPERIMENTAL SECTION

Analytical System. An air or gas stream is sampled and analyzed using an analytical system that was developed earlier[4] and is illustrated in Figure 1. After passing through a Nafion dryer, the sample air is drawn through the cryotrap via an eight-port valve (Valco, Houston, TX) by a vacuum pump (KNF Neuberger, Freiburg, Germany). The flow rate at STP is measured by a mass

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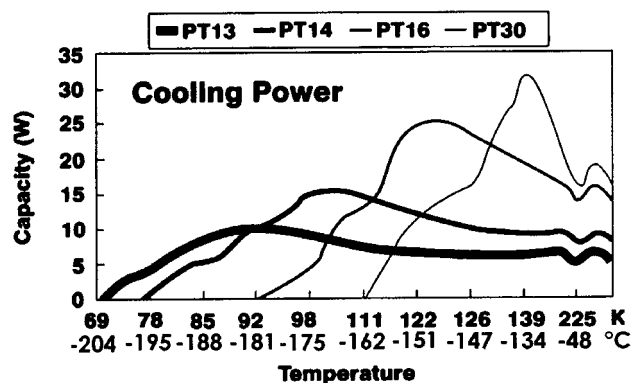
Figure 2. Temperature dependence of the Cryotiger's cooling power for different gas blends. The gas used here was PT16. Reproduced with permission of APG Cryogenics Ltd.

flow controller (FC280S, Tylan, Eching, Germany) after the exit of the eight-port valve. When the valve is switched from "sampling" to "inject" position ($^1/_4$ turn), the helium carrier gas is directed through the trap into a gas chromatograph (DANI 8500) equipped with a fluorinated ethylene propylene (FEP) packed column (1.8 m long, i.d. 1.6 mm, packed with 60/80 MeSH Carbopack B/1.5% XE 60/1.0% H_3PO_4, Supelco), and a flame photometric detector (FPD, Hewlett-Packard). In the original design, the cryotrap consists of a glass-lined steel tube (length 20 cm, i.d. 2 mm) filled with glass wool and cooled with liquid argon from a pressurized dewar inside an evacuated glass tube. To eject the trapped analytes, the trap is heated by a 1-s pulse of current ($\sim$200 A at 1.5 V), which almost instantaneously raises the temperature inside the empty trap to over 100 °C.

Cooling Unit. The Cryotiger (APD Cryogenics, Allentown, PA) refrigerator consists of a closed-cycle cold end, compressor, and two gas lines. The air-cooled compressor circulates the pressurized refrigerant to the cold head where the refrigerant absorbs heat after expansion to low pressure by a throttle device. The only requirement for operation is electricity with a power consumption of $\sim$500 W.

Different refrigerants are available (Figure 2), and for the one used here, the maximum cooling capacity is 24 W at −154 °C. By using a different refrigerant, the use of the system could be extended to applications that require temperatures as low as −203 °C (Figure 2).

Cold Trap Interface. For the new system, a glass-coated steel tube (Silcosteel, length 20 cm, o.d. 3.2 mm, i.d. 2.2 mm; Restek) filled with acid-washed dimethyldichlorosilane (DMCS)-treated mesh 45/60 Chromosorb W is used for cryogenic preconcentration. Chromosorb offers a higher surface area than glass wool and thus increases trapping efficiency.

The Cryotiger cold head is interfaced to this preconcentration trap and replaces the liquid argon cooling used in the original setup.[4] The interface between the trap and the Cryotiger (Figure 3) consists of three parts: a block of copper is screwed directly onto the Cryotiger cold head. While copper is a very good heat conductor, the mass of the block buffers the heat pulse needed to eject the sample from the trap so that the heat load on the cold head does not exceed its cooling capacity. A 7-cm-long, 1-cm-thick aluminum tube is used to expand the actively cooled surface so that the trap is effectively cooled over a length of 7 cm. Silicon tape (0.3 mm thick) between the aluminum and the trap is used to electrically isolate the trap from the cooling block and to regulate the heat transfer, so that the trap is still cooled effectively but the heat pulse to eject the sample is not conducted away from the trap too quickly. Small amounts of silicon grease (Dow Corning, Midland, MI) are applied where the surfaces of the different parts touch to ensure a uniform heat transfer. Temperatures at the copper block and the aluminum tube are −170 and −150 °C, respectively, measured using chromel alumel thermocouples.

The entire cold head and interface are placed inside a vacuum chamber pumped by a turbomolecular pump (TMH-64, Balzers, Liechtenstein) to maintain a pressure of less that 10^{-4} Torr needed to operate the Cryotiger. On each side, the trap is fed into the vacuum chamber through a piece of poly(tetrafluoroethylene) (PTFE) tubing (o.d. 6.4 mm, i.d. 4.0 mm) tightened using steel
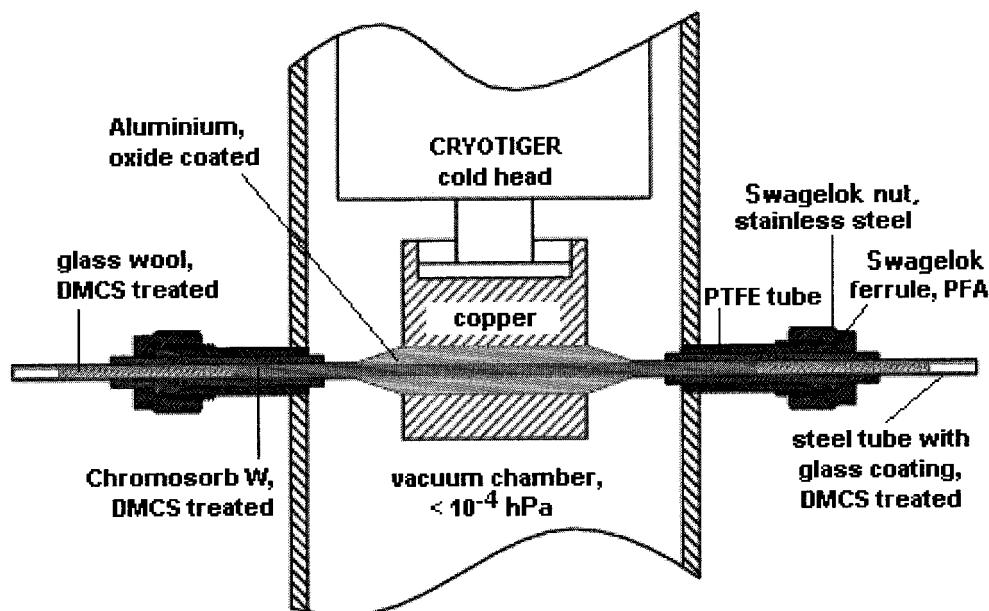

Figure 3. Schematic drawing of the interface between the trap and the Cryotiger cooling unit.
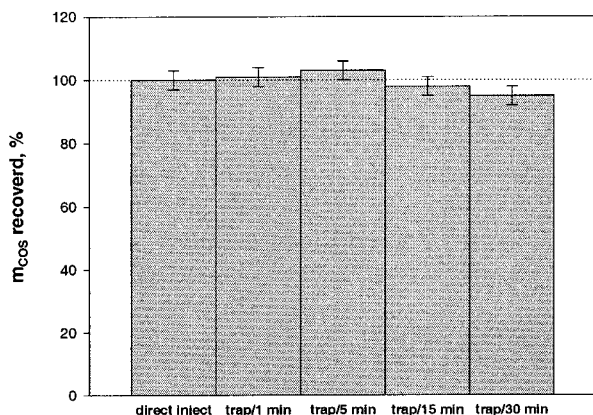
Figure 4. Recovery of COS by the cryogenic trap. Error bars indicate the uncertainty in the preparation of the sample (see text), which was always greater than variability of repetitive samples.

screw connectors (Swagelok, Frankfurt, Germany). The PTFE ensures electrical isolation from the vacuum chamber.

Efficiency Test and Calibrations. To test the efficiency of the new trap, discrete samples containing a specified amount of COS were either injected directly onto the chromatographic column or fed into a stream of COS free air flowing through the trap for varying amounts of time. Samples were prepared by filling a silanized glass loop of known volume with air enriched with COS from a permeation device (Vici Metronics, Houston, TX) kept in a thermostated chamber. As the volume of the loop and the COS permeation rate can be assumed constant over the experiment, the relative error in the amount of COS contained in a sample is equivalent to the relative error in the total air flow rate through the loop, which was 3%.

Calibration standards are prepared by gas dilution, using the aforementioned permeation device as a source of COS, and fed directly into the sampling line. Accuracy can be deduced from the uncertainties in the calibration curve; reproducibility is determined from repeated measurements on the same standard.

RESULTS

Figure 4 shows the recovery of COS by the trap, defining the result for the sample injected directly onto the column as 100%. Variability for each condition is always smaller than the 3% error introduced by the sample preparation. Only for long trapping times

(30 min) is a small loss of COS (<5%) by the trapping procedure observed.

Accuracy and precision at typical ambient COS concentrations are both better than 2%. The system has successfully been used for ship-based measurements of atmospheric and dissolved COS[5] and for laboratory studies on plant uptake of COS.[6] In the course of these experiments, the system has been running in continuous operation for several months.

CONCLUSIONS

The design of the cryogenic trap described here is rugged, is essentially maintenance free, and provides an effective means of analyte trapping at temperatures around −150 °C with electricity being the only requirement for operation. For trapping times up to 30 min, sample recovery is greater than 95%. With the novel trap integrated in the analytical system described above, fully automated measurements over an extended period with a good analytical performance are possible.

The system described here has been optimized for analyis of COS, but simple modifications could make it a useful method for a wide range of specific applications. By changing the Cryotiger refrigerant gas (Figure 2) and/or the insulation between the trap and the copper block, different trapping temperatures as low as −200 °C could be reached. By adjusting the electrical current or the duration of the heat pulse, the ejection temperature can be set over a wide range (up to 375 °C for the trap we used, which is where the silanization of the Chromosorb W starts to break down), which allows for simultaneous analysis of compounds with very different boiling points. Because analytes are trapped prior to the GC column, the cryotrapping unit can easily be used with different GC configurations and with other analytical techniques such as spectroscopy or mass spectrometry.

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