Microporous Oxides Science and Technology, L.L.C.
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In-Line Purification of Carbon Dioxide Used in SFE and SFC by Thermal Oxidation

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Introduction

Supercritical fluid extraction (SFE) and supercritical fluid chromatography (SFC) are often compromised by trace impurities present in solvent/mobile-phase carbon dioxide (CO_2). These impurities, commonly used as lubricants in the specialty gas industry,[1] can produce significant background levels, increasing limits of detection and quantification. This problem is especially severe when using electron capture detection (ECD) for trace analyte concentrations.[2-6] With SFE, these contaminants can also restrict the amount of CO_2 that can be used, possibly limiting the extraction efficiency of the technique.

Alternatively, high purity CO_2 can be purchased; however, the costs are significant. Also, contaminant build-up may not be sufficiently mitigated when long dynamic SFE analyses are necessary, or when performing supercritical fluid extraction coupled to gas chromatography (SFE-GC). The purpose of this application note is to present qualitative results of an in-line thermal oxidation-based purification system (the **C O$_2$P**, pronounced “COP”) for cleaning CO_2 used in SFE and SFC.

Experimental Section

The **CO$_2$P**urifier was evaluated by testing three different grades of commercially available carbon dioxide: “Bone Dry grade” (99.8% minimum purity, $90 per cylinder-1.54ft^3), “SFC/SFE grade” (<1,000 ppt ECD responsive contaminants, $350 per cylinder-1.04 ft^3), and “SFE grade” (<10 ppt ECD responsive contaminants, $600 per cylinder—1.04 ft^3). All cylinders were equipped with a helium pad and full length eductor tube.

Each grade was sampled (with and without in-line thermal oxidation purification at 300°C) by directly connecting the gas cylinder to a 150 μm o.d. x 15 μm ID fused silica restrictor, and passing the restrictor through the split/splitless injection port of a gas chromatograph (GC) directly into a DB-5 capillary column (30 m x 0.25 mm, 0.25 μm film thickness).

During sampling, the flow of hydrogen (H_2) carrier gas was stopped, and CO_2 was routed into the GC. Cylinder pressure (~100 atm) alone was sufficient to move CO_2 through the system for 30 minutes at a flow rate of 10-20 mL/min (gaseous). The GC injection port and oven were maintained at 30°C.

After a specified period of time, CO_2 flow was stopped and H_2 flow was resumed (at a velocity of approximately 60 cm/sec). After a 2 minute equilibration, a GC run was performed as follows: initial temperature 30°C, 50°C/min to 90°C, 5°C/min to 240°C, 10°C/min to 300°C, hold for 25 minutes at 300°C. The ^{63}Ni electron capture detector was maintained at a temperature of 330°C with flow rate of make-up gas (N_2) at 30 mL/min.

Results and Discussion

Chromatograms of unpurified Bone Dry grade (A), unpurified SFC/SFE grade (B), unpurified SFE grade (C), and **C O$_2$P**urified Bone Dry grade (D) are given in Figure 1. As shown, Bone Dry grade is cleaned to a higher purity than either SFE or SFC/SFE grade without purification.

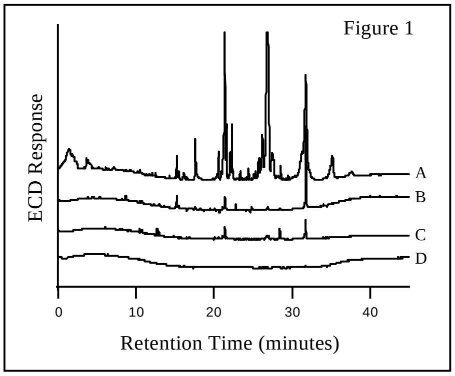
Figure 1

In addition to direct sampling from each of the CO_2 cylinders, higher pressure, higher flow rate off-line SFE experiments (50°C and 300 atm) were performed with the Bone Dry grade. Samples (~200g CO_2) were passed through the **C O$_2$P**urifier (maintained at 300°C) for 2 hours at a flow rate of 2 mL/min (~600 mL/min gaseous). The **C O$_2$P** was placed in-line between the CO_2 cylinder and the SFE pump. Contaminants were collected on a solid phase adsorbent trap and subsequently eluted with 5 mL hexane. The extracts were concentrated to a volume of 1 mL and analyzed by GC using the previously stated conditions (2μL splitless injection). Long-term purification of the Bone Dry grade showed no noticeable ECD-responding contamination even at these higher flow rate and pressure conditions.

Conclusions

Using an in-line thermal oxidation-based purification system (the **C O$_2$P**), minimum purity Bone Dry CO_2 has been purified to levels cleaner than the highest purity, most expensive CO_2 available. Previously prohibitive ECD responsive contamination has been reduced to non-detectable levels, even with 2 hour supercritical fluid extraction at relatively high flow rates (~1 L/min gaseous). In addition to lower limits of detection and quantification, significant cost savings can be realized using the **C O$_2$P** with inexpensive, low purity CO_2 in place of much more expensive, high purity CO_2.

References

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