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In-Line Catalytic Purification of Carbon Dioxide Used in Analytical-Scale Supercritical Fluid Extraction

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Supercritical fluid extraction analyses are often compromised by trace impurities present in the solvent carbon dioxide. These impurities, commonly used as lubricants in the specialty gas industry, can produce significant background levels, increasing limits of detection and quantification. This problem is especially severe when electron capture detection (ECD) is used for trace concentrations of analytes (e.g., polychlorinated biphenyls and chlorinated pesticides). In this study, an in-line catalyst-based purification system was successfully employed to remove ECD-responsive contaminants from CO_2. Low-purity (98%) "Bone Dry" CO_2 was purified to levels cleaner than a very-high-purity grade of CO_2 specified at less than 10 ppt ECD-responsive contaminants. Purification was successfully applied to extremely sensitive on-column experiments as well as higher flow rate off-line experiments. In addition to lowering limits of detection and quantification, significant cost savings can be realized by purifying inexpensive, low-purity CO_2 instead of relying on much more expensive, prepurified CO_2.

Analytical-scale supercritical fluid extraction (SFE) has received considerable attention in the past 15 years as a sample preparation technique.[1−3] SFE has shown the ability to achieve analyte recoveries that compare well with traditional Soxhlet and sonication methods.[4−8] In addition, SFE can be 10−50 times faster than traditional extraction techniques and eliminates hazardous organic solvents and their safety and disposal concerns.

Supercritical fluid extraction is often performed "off-line", or separate from subsequent separation and detection steps (e.g., gas chromatography, GC). Off-line SFE usually involves injecting 1−5 μL out of a total extract volume of 1−5 mL into the GC for quantification, thereby utilizing only ∼0.1% of the total sampled analytes. Consequently, the overall method sensitivity for off-line SFE is similar to traditional extraction methods.

Alternatively, SFE can be performed "on-line", or coupled directly to GC.[9,10] Similar to conventional GC, on-line SFE-GC can be performed either "split" or "on-column". Split SFE-GC offers advantages such as reliability, simplicity, and the ability to analyze wet or dirty samples.[10] However, depending on the split ratio, sensitivity enhancement over off-line SFE (or conventional methods) is not great. Conversely, with on-column SFE-GC, all of the extracted analytes are cryofocused at the head of the capillary column. This can be achieved by inserting the restrictor directly into the GC column (typically using an on-column injection port) or by using an intermediate trapping/desorption system. With on-column SFE-GC, the entire extract is utilized (i.e., 100% of the sampled analytes are transferred to the GC and are detected). Therefore, on-column SFE-GC can potentially increase the overall method sensitivity by several orders of magnitude. These gains can translate into smaller sample sizes, lower detection and quantification limits, or both.

Unfortunately, on-column SFE-GC has had limited application due to impurities present in the specialty CO_2 solvent. These contaminants, commonly used as lubricants in the specialty gas industry,[11] are concentrated along with analytes of interest and can interfere with subsequent GC analyses. This problem is especially severe using electron capture detection (ECD) for trace analyte concentrations.[12−16] These contaminants can also restrict the amount of CO_2 that can be used, possibly limiting the extraction efficiency of the technique. High-purity CO_2 can be purchased at considerable expense; however, contaminant buildup may still not be sufficiently mitigated when on-column SFE-GC is performed.[16]

Recently, Noll et al.[16] identified the ECD-responsive CO_2 contamination as chlorofluorocarbon grease, a mixture of oligo-

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mers of chlorotrifluoroethylene (CTFE). In this study, an in-line catalyst-based purification system was successfully employed to remove these ECD-responsive contaminants from specialty CO_2. Experiments were performed with extremely sensitive on-column sampling as well as higher flow rate off-line sampling. The mechanism for contaminant removal was also addressed.

EXPERIMENTAL SECTION

Evaluation of the catalyst-based purification system involved testing two different grades of commercially available CO_2: "Bone Dry" grade (98%, ECD-responsive contaminants not specified) and SFE grade (<10 ppt ECD-responsive contaminants). Both grades were analyzed with and without in-line catalyst purification as described below. Cylinders were equipped with a helium pad and full-length eductor tube.

Catalytic Reactor. Purification of the CO_2 samples was achieved using a microporous titania-based particulate catalyst (Microporous Oxides Science and Technology, Oregon, WI), that was modified from Fu et al.[17] The catalyst material has a surface area of ~250 m^2/g. The catalyst was packed into a stainless steel reaction cell that was inserted into a temperature-controlled chamber.

On-Column Sampling. Sampling of both the Bone Dry and SFE grades of CO_2 (with and without in-line catalytic purification) was performed on-column to achieve maximum sensitivity and to eliminate the effects of any other procedural steps. For unpurified samples, CO_2 flowed from the cylinder through a length of $^1/_{16}$ in. stainless steel tubing and into a fused-silica restrictor (150 μm o.d. × 15 μm i.d., Polymicro Technologies, Phoenix, AZ). The stainless steel tubing was attached to the restrictor using a $^1/_{16}$ in. × $^1/_{16}$ in. union (Valco Instruments, Houston, TX) and a $^1/_{16}$ in. (0.3 mm hole) 85% Vespel, 15% graphite ferrule (Alltech Associates, Inc., Deerfield, IL). For purified samples, the catalytic reactor (2.0 g of catalyst, heated to 300 °C) was placed in-line between the cylinder and the restrictor. For all samples, the restrictor was inserted through a prepunctured septum and split/splitless injection port of a Hewlett-Packard 5890A GC, directly into a DB-5 capillary column (J&W Scientific, Folsom, CA; 30 m × 0.25 mm i.d., 0.25 μm film thickness). (In practice, the capillary column was first disconnected from the injection port. The restrictor was then fed down through the septum and injection port into the GC oven. The restrictor was then cut to allow an insertion of 2 cm into the column. Finally, the column was threaded over the restrictor and reattached to the injection port.)

During sampling of the CO_2, the flow of chromatographic carrier gas was stopped and CO_2 was routed into the GC as described above. The GC injection port and oven temperatures were set at 30 °C; however, due to the expansion of CO_2, the actual temperature at the outlet of the restrictor was probably significantly lower. Cylinder pressure (~100 atm) alone was sufficient to move the CO_2 through the system for 30 min at 10−20 mL/min (measured at the GC outlet using a volumetric flowmeter). This flow rate was chosen in order to maintain good chromatographic peak shapes. After sampling, CO_2 flow was stopped and carrier gas flow was resumed (H_2, at 60 cm/s). After a 2 min equilibration, a normal 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, and retained for 25 min at 300 °C. The ^{63}Ni electron capture detector was maintained at a temperature of 330 °C with 30 mL/min N_2 makeup gas.

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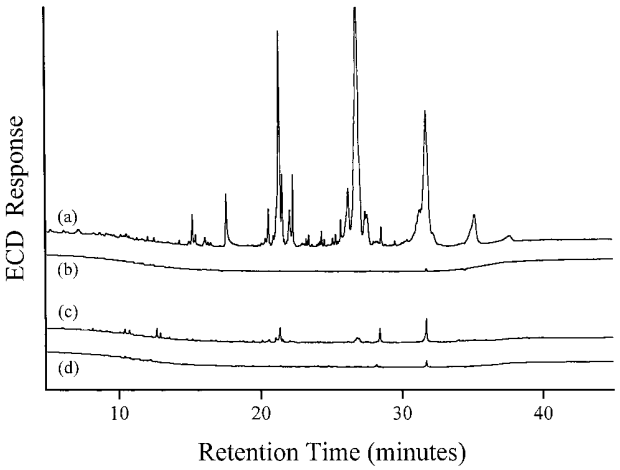

Figure 1. Chromatograms of CO_2 contamination collected on-column: (a) Bone Dry grade directly from the cylinder, (b) Bone Dry grade with catalytic purification, (c) SFE grade directly from the cylinder, and (d) SFE grade with catalytic purification. See text for experimental parameters.

Off-Line Sampling. Off-line sampling was also performed with the Bone Dry grade of CO_2 to assess catalyst performance at a higher volumetric flow rate and to attempt quantification of the contaminants. Samples were collected both with and without catalytic purification (0.7 g of catalyst, heated to 250 °C) by routing the flow of CO_2 through a variable restriction device and into an adsorption trap filled with precleaned Florisil (60−100 mesh, U.S. Silica Co.). As before, cylinder pressure was sufficient to enable flow through the system. Samples were collected for 1 h at a flow rate of 250 mL/min (measured at the Florisil trap outlet using a volumetric flowmeter). After collection, CO_2 flow was stopped and 4 mL of hexane (Omnisolve glass-distilled, EM Science, Gibbstown, NJ) was passed through the Florisil trap. PCB congeners 30 and 204 were subsequently added as internal standards. A procedural blank was obtained by rinsing the adsorbent trap, filled with precleaned Florisil, with 4 mL of hexane and processing as above. Off-line samples were subsequently analyzed using a second Hewlett-Packard 5890A GC with ECD. The oven program was as follows: initial temperature 90 °C (retained for 1.2 min), 5 °C/min to 240 °C, 10 °C/min to 300 °C, and retained for 25 min at 300 °C. All other GC settings were as described above. Quantification of the ECD-responsive contamination was performed as in Noll et al.[16]

RESULTS AND DISCUSSION

On-Column Samples. On-column chromatograms of Bone Dry and SFE grades of CO_2 with and without catalyst purification at 300 °C are shown in Figure 1. For both grades, catalyst purification reduces the ECD-responsive CTFE grease contamination to very low levels; the most dramatic reduction is for minimum-purity Bone Dry grade as shown in traces a and b of Figure 1. In fact, the Bone Dry grade of CO_2 is cleaned to an even higher purity than the SFE grade without catalyst purification.

Off-Line Samples. Additionally, higher flow rate (250 mL/min) off-line samples were obtained with the Bone Dry cylinder. Quantification of the unpurified samples yielded an average concentration of 85.9 ppb (ng of CTFE grease/g of CO_2), with a relative standard deviation of 8.2% and a 95% confidence interval of 17.5 ppb ($n = 3$). Using the catalyst purifier, CTFE grease

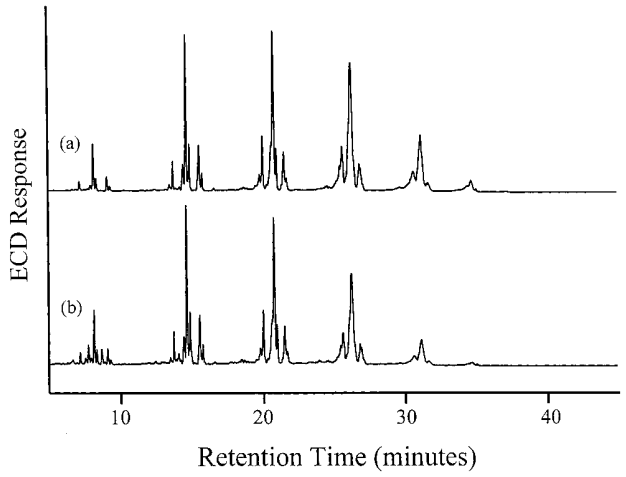

Figure 2. Chromatograms of Bone Dry grade CO_2 contamination collected off-line (a) directly from the cylinder and (b) passed through a heated bed of silica gel. See text for experimental parameters.

contamination present in the Bone Dry CO_2 was reduced to levels below our instrumental detection capabilities (i.e., all peaks that were present above background in the purified sample were also present in the procedural blank); therefore, quantification could not be performed. Subsequent off-line collection of the purified Bone Dry CO_2 for 2 h at a flow rate of 600 mL/min (measured as discussed above) still resulted in chromatograms that were indistinguishable from procedural blanks. In addition, the catalytic purifier has currently been operating (with Bone Dry CO_2, at a reactor temperature of 250 °C) with an off-line SFE system for the past 6−12 months with no noticeable decrease in catalytic performance.

An additional experiment was performed to rule out the unlikely possibility that the contaminants were merely adsorbing onto the surface of the catalyst material. A reactor cell was filled with 0.4 g of silica gel (a noncatalytic absorbent material) with a particle size and surface area (∼300 m^2/g) similar to that of the catalyst. The reactor cell was then heated to 250 °C, placed in-line between the CO_2 cylinder and the restrictor, and contacted with Bone Dry CO_2 for a brief period of time to enable saturation of the adsorptive sites with contamination. Off-line samples were subsequently collected (as described above) and compared to the unpurified CO_2. The Bone Dry CO_2 that was passed through the silica gel exhibited contamination on the same order of magnitude as the unpurified Bone Dry CO_2 (see Figure 2). The two chromatograms are virtually indistinguishable by visual inspection.

Interestingly, CO_2 that was passed through the bed of silica gel was slightly enriched in earlier eluting contaminants and slightly depleted in later eluting contaminants. This result could be explained two different ways. One possible explanation may be the occurrence of a "chromatographic effect", whereby the heavier contaminant compounds are retained longer by the silica gel than the lighter compounds. Samples obtained at the outlet of the silica gel would therefore be enriched in the less retained, lighter contaminant compounds. In an alternative explanation, the higher molecular weight polymer-chained CTFE molecules may simply be undergoing noncatalytically thermolytic depolymerization[18−20] to smaller oligomers that are still trapped, analyzed, and detected with the sampling method. Noncatalytic thermal degradation of CTFE polymers to CTFE monomer occurs at higher temperatures (360−390 °C[18,19]) than used here; however, some thermal degradation has been reported at 275−300 °C.[20] In either case, the *total* contamination present in the silica gel-treated CO_2 (71.2 ppb) was still within the 95% confidence interval reported above for the unpurified Bone Dry CO_2. Thus, even if some minimal noncatalytic thermal degradation is occurring at 250 °C, the total CTFE grease contamination is virtually unchanged, and the degradation products continue to interfere with subsequent GC-ECD analyses.

The complete removal of the CTFE grease contaminants from the CO_2 stream by the catalyst material appears to be the result of a truly catalytic process, rather than simply adsorption of the contaminants onto the catalyst surface or noncatalytic thermal degradation. Although the exact mechanism for the catalytic process is not known, two possibilities exist. The most likely possibility is that the contaminants (present only at ppb levels) are reacting with residual oxygen present in the CO_2 stream; *catalytic oxidation* thus results in the removal of the impurities. Alternatively, *catalytic depolymerization* of the CTFE polymers may be occurring at 250 °C, resulting in the generation of gaseous CTFE monomer molecules (MW = 116.47, bp = −26.2 °C) that are not trapped by the methods used here.

CONCLUSIONS

Using an in-line catalyst-based purification system, minimum-purity Bone Dry CO_2 has been purified to levels cleaner than the highest purity, most expensive CO_2 commercially available. Previously prohibitive ECD-responsive contamination has been reduced to nondetectable levels, producing CO_2 that is clean enough for trace analysis using on-column SFE-GC with ECD. Decreased limits of detection and quantification can be realized using this treatment method with inexpensive, low-purity CO_2 at a significant cost savings (potentially hundreds of dollars per cylinder) in place of much more expensive, high-purity CO_2. The catalytic purification system simply requires a heated catalyst bed (250 °C) and inlet and outlet tubing connections. Depending on the flow rate, active cooling of the effluent CO_2 stream may also be required. Once the system is in place, there is virtually no additional time requirement (other than the time required to heat the catalyst bed) compared to the use of commercially available high-purity CO_2.

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