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TECHNICAL NOTES

Recovery of Submilligram Quantities of Carbon Dioxide from Gas Streams by Molecular Sieve for Subsequent Determination of Isotopic (¹³C and ¹⁴C) Natural Abundances

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INTRODUCTION

Quantitative recovery and isotopic analysis of CO₂ generated from organic and inorganic carbon is important for a variety of natural sample types. For example, the two most commonly used techniques for the oxidation of organic carbon to CO₂ are the sealed-tube method¹ and various modifications of the flow-through combustion method.² While both methods ultimately depend upon the presence of O₂ for the oxidation process, the sealed-tube method has been the method of choice for the subsequent recovery and isotopic analysis of CO₂. This is due to the relative ease with which CO₂ (sublimation point = -78.5 °C at 760 mmHg pressure) can be cryogenically removed from an otherwise noncondensable, static (i.e., non-flowing) gas mixture under vacuum. This concept has been improved upon through the use of variable-temperature cryogenic traps (VTTs)^{3,4} which allow gas components having different melting points to be sequentially frozen out and distilled off for collection of essentially pure product. In contrast, CO₂ contained in carrier gas streams is generally difficult to collect at atmospheric pressure following organic carbon combustion since this usually entails using O₂ as both the oxidant and the carrier gas. Cryogenic collection of CO₂ at liquid nitrogen temperature (bp -195.8 °C) from an O₂ stream results in the condensation of liquid O₂ (bp -183.0°C), a potentially hazardous situation, and possibly in incomplete CO₂ recovery. Pumping the liquified O₂ away under vacuum, or trapping the CO₂ from the O₂ stream at temperatures below

the boiling point of O₂ using VTTs, can also result in incomplete recovery and isotopic fractionation of CO₂. In fact, even when N₂ is used as the carrier gas at atmospheric pressure and liquid nitrogen temperature, intermittent condensation of the N₂ stream may occur,⁵ though this is much less severe than for O₂. Finally, systems which are designed to collect CO₂ from gas streams (especially O₂) cryogenically or using partial vacuums can attain considerable complexity.

A method is therefore needed which allows CO₂ to be quantitatively recovered from O₂ and N₂ gas streams at atmospheric pressure. For isotope studies, a further requirement is that no fractionation of the carbon isotopes in the CO₂ occurs. This led us to develop a simple, convenient method which is based on the highly selective absorptive properties of aluminosilicate molecular sieves for different gases. While molecular sieves have been employed to a limited extent in some commercial organic carbon analyzers, in some cases for δ¹³C determinations (e.g., see ref 6), a thorough assessment of the analytical capabilities of sieves has, to our knowledge, not been made. The method presented here has a low associated blank (<0.02 μmol of C), is robust over a wide range of O₂ and N₂ carrier gas flows (at least 100-2000 cm³·min⁻¹) and quantities of CO₂ (at least 0.3-50 μmol of C), and is nonfractionating with respect to carbon isotopic (¹³C and ¹⁴C) natural abundances. Molecular sieves should have a variety of applications for CO₂ quantification and isotopic analysis.

EXPERIMENTAL SECTION

The specific molecular sieve used in these studies was a synthetic sodium aluminosilicate zeolite having the molecular formula

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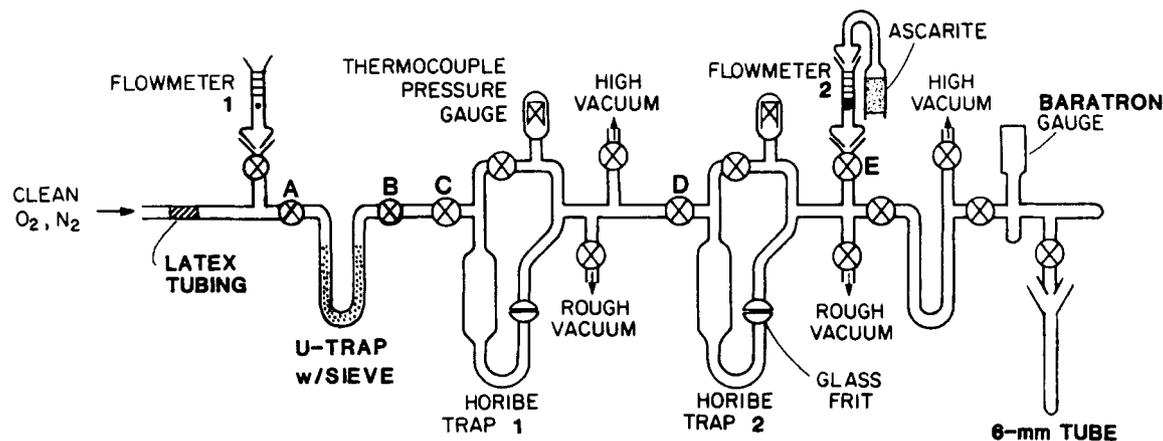


Figure 1. Schematic drawing of the gas flow/vacuum line system used in the present study for evaluation of Type 13X molecular sieve. The flow of gases in the system is from left to right.

$\text{Na}_2\text{OAl}_2\text{O}_3\text{SiO}_2$ (Type 13X, $1/16$ -in. pellets, Linde Division, Union Carbide Corporation, Danbury, CT). The sieve aperture is 10 Å in diameter, while the molecular diameters of CO_2 , O_2 , and N_2 are 3.34, 2.98, and 3.15 Å, respectively. The number of molecules of a specific compound which are retained in the sieve cavities via the sieve apertures is strongly dependent on both the molecular diameter and the temperature of the sieve.⁷ Molecular sieves are selective for specific gas molecules not only on the basis of pore size but also on the basis of molecular polarity and boiling point. In the case of Type 13X, the Na^+ -containing sieve is strongly polar, resulting in a preferential retention of CO_2 over other, less polar gases (e.g., O_2 and N_2). It is likewise imperative that molecules which could potentially displace CO_2 (e.g., H_2O) be prevented from entering the sieve. Type 13X is commonly used in industrial applications for the removal of CO_2 gas and H_2O vapor from hydrocarbon gas mixtures.

To evaluate the molecular sieve for quantitative collection and release of CO_2 , as well as the isotopic fidelity of the trapped and released CO_2 , a sieve trap was interfaced to a gas flow/vacuum extraction line. The components of the system in which Type 13X was used are shown in Figure 1. The quartz U-tube (dimensions: height, 150 mm; i.d., 9 mm; o.d., 12 mm) contains approximately 12 g of sieve which is immobilized by plugging the tube with prebaked quartz wool. The U-tube has sealing o-ring stopcocks at each end which allow it to be removed from the main line as needed without exposing the sieve to air. The sieve should be exposed to air for a minimum of time when transferring it to the U-tube in order that adsorption and desorption of atmospheric gases and contaminants are minimized. Water vapor is the most deleterious of these components, and it may reduce the efficiency of the sieve if exposure is chronic (G. Rand, personal communication). When the unit is attached to other instrumentation a trap of magnesium perchlorate upstream from the sieve trap has been found to be adequate for eliminating the H_2O before it reaches the molecular sieve. Care should also be taken to keep the sieve free of organic contaminants during handling because of the potential for their slow oxidation at elevated temperatures (see below).

When a new batch of sieve is used it should be conditioned for at least 24 h by opening the U-tube to full vacuum (10^{-6} atm) while heating at 550 °C with a heating jacket (Glas-Col, Terre Haute, IN). This temperature is well below that which purportedly causes degradation of the zeolite (~ 700 °C; G. Rand, personal communication), but it is high enough to eliminate absorbed CO_2 and H_2O from the sieve and to volatilize and combust any initially adsorbed organic contaminants. In operation, the sieve is allowed to equilibrate at room temperature (22–25 °C) before CO_2 collection. At least temperatures, O_2 and N_2 molecules pass freely through the sieve apertures and occupy very little of the sieve's total available cavity space.⁷ Since the sieve will normally be at full vacuum following the analysis of a prior sample, it is then brought to atmospheric pressure by closing the system to vacuum and then introducing ultra-high-purity O_2 or N_2 ($400 \text{ cm}^3 \cdot \text{min}^{-1}$) into the U-tube by slowly opening the upstream stopcock A. The gas is then allowed to flow through the remainder of the system

and to vent by opening stopcocks B–E. At this point, if the sieve is to be used for collecting CO_2 from a remote instrument, it may be isolated by closing stopcocks A and B, and flowmeter 1 and the U-tube are removed as a unit from the flow/vacuum line. For purposes of this study, however, it was maintained intact on the flow/vacuum line.

The recovery of CO_2 from O_2 and N_2 streams was evaluated as follows. The carrier gas was adjusted to the desired flow rate with the molecular sieve trap maintained at room temperature. A quantity of pure CO_2 of known isotopic composition was injected through heavy-walled latex rubber tubing using a precision microliter syringe (Micrometrics, Shorewood, IL). The total time for all injections was 2.0 min. A period of 5 min was allowed to elapse after injection, and flow was then stopped by closing stopcocks A and E. The entire system was then brought to full vacuum. Horibe trap 1 was immersed in a bath consisting of dry ice in 2-propanol (-78.5 °C) to serve as a water trap. Horibe trap 2 was immersed in liquid nitrogen to serve as the CO_2 trap. The Horibe traps were employed here because their design, with increased dead volume for greater residence time and glass frits for increased surface area, allow for quantitative collection of CO_2 even under full dynamic vacuum.⁸ The stopcocks to vacuum were then closed so that the system was under static vacuum. Preliminary tests of the retention efficiency of the sieve demonstrated that no CO_2 leaked past the U-tube following injection and none desorbed from the sieve while at room temperature under full dynamic vacuum for at least 1 h. The heating jacket was then placed around the U-tube, and the CO_2 was transferred to Horibe trap 2. Following transfer, Horibe trap 2 was evacuated again, and its contents were cryogenically transferred to the measured volume under static vacuum. The volume of gas was measured using a Baratron absolute pressure transducer (MKS Instruments, Andover, MA) which had previously been calibrated with known CO_2 gas standards.

For $\delta^{13}\text{C}$ determinations the above procedure was followed, and CO_2 standard gas samples were cryogenically collected in 6-mm glass tubing which was flame-sealed. The $\delta^{13}\text{C}$ of the samples was measured with a Nuclide 6-60RMS mass spectrometer. For $\Delta^{14}\text{C}$ determinations, oceanic humic matter of known $\Delta^{14}\text{C}$ was dissolved in ultra-high-purity artificial seawater and combusted to CO_2 using a high-temperature total organic carbon analyzer. The unit was interfaced to the sieve U-tube which trapped the CO_2 from the O_2 gas stream. The CO_2 was purified and collected as above for subsequent $\Delta^{14}\text{C}$ analysis by tandem accelerator mass spectrometry.

RESULTS AND DISCUSSION

A wide range of carrier gas flow rates and quantities of CO_2 was used to assess the conditions under which Type 13X sieve could be used. In addition, various operating parameters (desorption temperature, desorption time) were also evaluated in order to develop an optimized protocol for routine use of the sieve. Initial tests using O_2 and N_2 as carrier gases revealed that recoveries of CO_2 were identical using these two gases.

Table I. Recoveries (%) of Standard Amounts of CO₂ from O₂ Stream at Different Flow Rates Using Type 13X Molecular Sieve^a

O ₂ flow rate (cm ³ ·min ⁻¹)	recovery (%)
150	100.0
3-h O ₂ flow, then CO ₂ injection	100.0
CO ₂ injection, then 3-h O ₂ flow	100.0
420	100.7
1000	99.3
2000	100.0

^aCO₂ (250 μL) was injected over a 2-min interval. Standard deviation of replicate trials was ±1.0%.

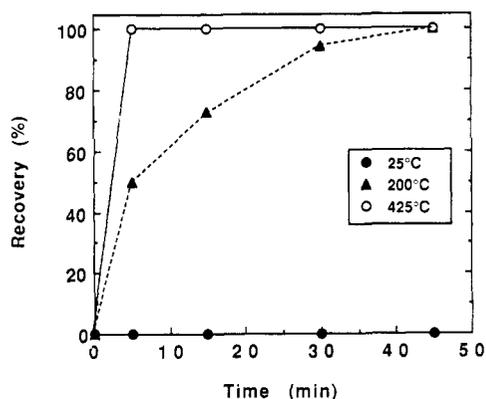


Figure 2. Recovery of standard CO₂ gas from sieve trap as a function of time while held at room temperature (25 °C) and during heating at 200 and 425 °C. The CO₂ (250 μL) was added by 2.0-min injection to O₂ stream flowing at 150 cm³·min⁻¹. Standard deviation of replicate runs was ±1%.

Subsequently, O₂ was used as the carrier gas for further experimental evaluation both because it is normally used for flow-through organic carbon combustion and because it is more problematic in cryogenic applications. The system blank using Type 13X was insignificant (always <0.02 μmol of C), and hence sample values required no correction.

The CO₂ was trapped with 100% efficiency by Type 13X molecular sieve for quantities of CO₂ ranging over 2 orders of magnitude (0.3–50 μmol, $r^2 = 1.000$, $n = 12$). The trapping efficiency of CO₂ gas was independent of the flow rate of O₂ through the sieve and was also 100% in all cases (Table I). This demonstrates the extremely high affinity of Type 13X for CO₂ since the residence time of gas in the U-tube was less than 1 s at the greatest flow rate used here (2000 cm³·min⁻¹). The equivalent range of CO₂ concentrations over all tests was 2–130 μmol per liter of carrier gas. The sieve retained 100% of the CO₂ (10 μmol) even when followed by prolonged periods (3 h) of continuous O₂ flow (Table I). The CO₂ was also retained with 100% efficiency when it was introduced to the sieve after the residence time of gas in the U-tube was less than 1 s at the greatest flow rate used here (2000 cm³·min⁻¹). The equivalent range of CO₂ concentrations over all tests was 2–130 μmol per liter of carrier gas. The sieve retained 100% of the CO₂ (10 μmol) even when followed by prolonged periods (3 h) of continuous O₂ flow (Table I). Therefore, applications which require extended periods of time to collect adequate amounts of CO₂ for a given analysis are assured of quantitative recoveries.

The time dependence of CO₂ release from Type 13X sieve under vacuum was evaluated at three temperatures (Figure 2). At room temperature (25 °C), prolonged (1 h) application of full vacuum to the sieve trap resulted in no loss of absorbed CO₂. At 200 °C, 100% release took up to 45 min. However, at 425 °C, complete release was achieved within 5 min of heating. For most applications, rapid release is preferable in order to avoid potential isotopic fractionations resulting from the kinetic effects of slow release. We routinely heat the sieve rapidly to 425 °C by maintaining the heating jacket at this temperature, even when it is not around the U-tube. Although the sieve can be heated to ~700 °C, its structure may begin

Table II. Isotopic Signatures of Injected CO₂ Standard Gas (δ¹³C) and of CO₂ Derived from High-Temperature Flow-Through Combustion of Oceanic Humic Substances (Δ¹⁴C)^a

CO ₂ derivation	δ ¹³ C (‰)	Δ ¹⁴ C (‰)
standard gas injection		
known	-35.9 ± 0.2	-
sieve	-35.8 ± 0.1	-
oceanic humics combustion		
humic no. 161		
known	-	-387 ± 26
sieve	-	-374 ± 21
humic no. 151		
known	-	-495 ± 30
sieve	-	-509 ± 29

^aThe CO₂ was collected on Type 13X molecular sieve and subsequently purified for isotopic analysis (see text for details). Oxygen carrier gas flow rate was 150 cc·min⁻¹.

to break down at such elevated temperatures, resulting in a loss of trapping efficiency (G. Rand, personal communication). The lowest blanks are attained when the sieve is kept at 425 °C, especially when it is not being used for extended periods of time.

The stable isotope ratio of CO₂ trapped and released by the sieve was identical to that of the stock CO₂ (Table II). Triplicate injections of 10 μmol of CO₂ at an O₂ flow rate of 150 cm³·min⁻¹ yielded δ¹³C = -35.8 ± 0.1‰ while the known value of stock CO₂ was δ¹³C = -35.9 ± 0.2‰ indicating that fractionation of CO₂ upon passage through the sieve did not occur. Although stable isotope ratios were measured for 10-μmol samples of CO₂ only, accurate ratios are expected for lesser and greater quantities of CO₂ and at different flow rates since recoveries were 100% in all cases. However, for very small or very large amounts of CO₂ the accuracy of isotopic values should be checked against similarly sized known gas standards which have been processed through the sieve trap. When the sieve was interfaced to a high-temperature organic carbon analyzer with O₂ as the carrier gas, the Δ¹⁴C signatures of the CO₂ (8–10 μmol) derived from combustion of oceanic humic substances were indistinguishable from the known signatures determined by sealed-tube combustion (Table II). Thus, both δ¹³C and Δ¹⁴C may be accurately determined by collection of CO₂ from the gas stream using the sieve trap. It should also be noted that for these short-term collections the associated blank was insignificant.

The simplicity of the trap and the range of conditions over which Type 13X molecular sieve can be used provide several advantages over systems which use cryogenic collection of CO₂. The sieve can be used at atmospheric pressure and at the room temperature of most laboratories to collect CO₂ from either O₂ or N₂ (and possibly other gases) carrier gas streams. The upper limits examined in this study were 2000 cm³·min⁻¹ flow rate and 50 μmol of CO₂. These ranges may well be greater in the system used here but in any case could be expanded by using collection tubes which hold a greater volume and mass of sieve or by using multiple traps arrayed in series. Under very rigorous flow conditions or extremes in amounts of CO₂ collected, retention efficiencies, as well as stable isotope ratios, should be checked periodically to ensure that the capacity of the sieve is not exceeded. We have used a single batch of Type 13X in a U-type continuously for over 12 months with no signs of performance deterioration, resulting in significant savings in both cost and maintenance over cryogenic collection systems.

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Inverse Sampling Valve Interface for On-Line Process Monitoring with a Mass Spectrometer

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INTRODUCTION

Advances in analytical instrumentation have led to new designs and application of on-line, real-time process monitoring,¹⁻⁶ including methods which rely on chromatographic² or spectroscopic analysis.⁶⁻⁸ With the advent of less costly, compact, and less complex mass spectrometers,⁹ increasing efforts have been directed at developing on-line mass spectrometric techniques,¹⁰⁻¹⁹ because they offer both qualitative and quantitative information about the chemical process with high sensitivity.

Mass spectrometry is particularly suitable for sampling gaseous streams. Many applications of on-line gas chromatography-mass spectrometry interfaces¹⁰ have been reported. Additionally, direct gas sampling may be achieved by use of a pulsed electromagnetic valve connected to a mass spectrometer.^{11,12} The use of a pulsed valve with a Fourier transform ion cyclotron resonance mass spectrometer¹¹ or a quadrupole ion trap mass spectrometer¹² has proven effective for intermittent introduction of volatile components. More recently, several examples of mass spectrometric liquid sampling have been demonstrated. Most rely on atmospheric pressure ionization (API) sources¹³ or membrane separators¹⁴⁻¹⁹ to accommodate the potentially high gas load when a liquid is sampled into a vacuum. Unfortunately, API sources are mechanically complex and involve additional stages of differential pumping. Although the membrane-based devices are versatile and less complex, they exhibit long or variable response times due to slow diffusion of the analyte through the membrane.

In some cases, a more direct liquid-sampling system is preferred to a membrane interface, especially if quantitative sample transfer or faster response times are needed. Microliter quantities of liquid solutions can be introduced into a mass spectrometer via a conventional direct insertion probe,²⁰ but this technique involves use of a vacuum interlock and is not suitable for on-line continuous-monitoring applications. In this report, we demonstrate for the first time direct on-line monitoring of gas or liquid samples by using an inverse sampling valve coupled to a mass spectrometer.

Standard versus Inverse Liquid-Sampling Valves. *Standard Liquid Sampling.* Liquid-sampling valves such as those made by ABB²¹ or MAT²² operate on the principle of metering microliter quantities of a liquid into a carrier gas

stream and then vaporizing the liquid rapidly and completely into a gas chromatograph (GC). To our knowledge, these liquid-sampling valves have never been used to transfer samples directly to mass spectrometers. Figure 1 is a cross-sectional view of a portion of a MAT valve attached to a gas chromatograph. Liquid sample from the process stream is directed to the valve through port 1. The sample fills the grooved slot, 2, of the piston, 3, and is transferred to the heated vaporization zone, 4, upon actuation of the piston. The seals, 5, ensure that only sample in the slot ($\sim 1 \mu\text{L}$) is transferred. Hot carrier gas, 6, flashes the sample and directs it into the GC column, 7.

Inverse Sampling. Inverse sampling²³ is a recent modification of the liquid-sampling valve, wherein the heated vaporization section is removed and the remainder of the valve is welded to the vessel holding the material to be transferred. For our purposes, this vessel is a short welded section of 2-in. pipe, which serves as the sample chamber. The valve is further modified to expose one of its seals into the sample chamber. The liquid-transfer section of the standard valve becomes an evacuation chamber or vaporization section in the modified valve. Finally, the mode of operation is opposite to the standard liquid sample; i.e., the inject position becomes the load position and vice versa. The sampling piston captures sample from the chamber or process stream into its $1/4\text{-}\mu\text{L}$ groove while in the extended (load) position and transfers it in the retracted (inject) position. Transference takes place by evacuation of the sample-filled groove into the analytical instrument, with or without a supplementary carrier gas stream. When the sample is a liquid, the "vaporization zone" must be heated and a carrier gas is recommended. These added steps are unnecessary for gas samples.

The advantage of inverse sampling is that the valve can be attached directly to the process, obviating the need for divert streams or pumps. This sampler can be used for transference of any vaporizable substance and is particularly useful for molten streams which are ordinarily difficult to sample.

EXPERIMENTAL SECTION

Two spectrometers were used, a Finnigan quadrupole ion trap mass spectrometer (ITMS)²⁴ located at the University of Texas for gas sampling and a Finnigan 4600 quadrupole mass spectrometer located at Dow U.S.A. for liquid sampling. Pentachloropyridine (PCP) was obtained from Dow Chemical. All other