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All-metal collection system for preparative-scale gas chromatography Purification of low-boiling-point compounds

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Abstract

We describe a purification system based on a commercial preparative-scale gas chromatograph with a custom-designed condenser, collector, and fraction handling system. In our fraction collector design, all the wetted surfaces were either 316 stainless-steel or nickel. The collectors and the integrated gas-handling manifold were designed to be used down to liquid nitrogen temperature and up to 7 MPa of pressure to accommodate low-boiling-point compounds, such as refrigerants. The design, operation, and performance of this apparatus are presented.

1. Introduction

Inconsistent or irreproducible measurements of thermophysical and chemical properties are often due to impure samples. The effects of impurities in fluids can greatly exceed imperfections in instrumentation. Along with the continued need for better measurement techniques and for better analytical instrumentation, there exists a growing need for methods of preparing ultra-pure samples. This is especially true for low-boiling-point liquids that require special handling and for liquids that form azeotropes with other production by-products, since distillation techniques are impractical in these cases.

The speed-of-sound in a gas and the vapor pressure and viscosity of liquids are examples of thermophysical properties that are sensitive to the presence of certain impurities. When highly accurate measurements of these properties are desired, the purity of the sample must be high enough that either the uncertainty due to the impurities is below the sensitivity of the technique used, or that the perturbation due to impurities is accurately calculable. It is often the case that an impurity level of 0.1%, typical of many commercially available compounds, is sufficient to dominate the uncertainty of a measurement. Even if these impurities are identified and their concentrations measured (itself a time-consuming and expensive task), the properties of the impurities may not be known with sufficient accuracy to correct the measurements.

As an example, consider that commercially available pentafluoroethane (CF_3CHF_2; designated in the refrigeration industry as R125) contains a mole fraction of 0.15% chloropentafluoroethane (designated R115). The presence

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of this impurity lowers the speed of sound from pure R125 by 0.02%. If not accounted for, this impurity would increase the ideal-gas heat capacity deduced from speed-of-sound data by 0.4%. This impurity-related error would be an order of magnitude larger than the errors in "routine" speed-of-sound measurements [1].

R125 has a normal boiling point of −49°C, a vapor pressure of 1445 kPa (210 p.s.i.a.) at 27°C, and it forms an azeotrope with R115 near the composition mentioned above. These properties of R125 preclude the use of glass apparatus for handling it and conventional distillation techniques for purifying it.

Minor impurities can also have a major impact in the field of chemical kinetics. The reaction rate of an impurity with a free radical, such as OH, can exceed that of the pure chemical species by orders of magnitude. A 100 ppm impurity which reacts 1000 times faster than the main component leads to a 10% error in the measured reaction rate. Methyl chloroform, CH_3CCl_3, is an important compound that is used as a standard for the lifetime of chlorofluorocarbons in the atmosphere [2,3]. In the troposphere CH_3CCl_3 is attacked by OH, then further oxidized and eventually washed out before it reaches the stratosphere where it would deplete ozone. A common impurity in methyl chloroform is the alkene CH_2CCl_2 which reacts nearly 1000 times faster with OH. Careful attention must be paid to this and other trace impurities in the tested samples to exploit the 10% uncertainty in the current state-of-the-art kinetic measurements.

When sample purity is critical, materials compatibility becomes an important issue. PTFE tape, elastomer O-rings, and greases for joint seals are examples of common laboratory materials that must be avoided. Since many compounds are hygroscopic, contamination may also occur if the sample comes in contact with air and/or water.

Preparative-scale gas chromatography (prep-GC) is a well-known [4,5] separation method, with which high-purity ($>99.9\%$) compounds may be isolated from a mixture of substances that are otherwise difficult to separate [6]. For a comprehensive discussion of the design and performance of prep-GC systems, the reader is directed to the work by Conder and Purnell [7–10]. However, prep-GC techniques are not routinely used with low-boiling-point compounds [11] such as alternative refrigerants. Most commercial prep-GC systems have fraction collectors made of glass, which severely limit the working pressure range. In addition to pressure limitations, glass systems require elastomer and/or greased joints (which can contaminate the purified sample) to ensure proper seals.

In this paper, we describe a purification system based on a commercial prep-GC system with a custom-designed condenser, collector, and fraction handling system. The special design of this system is meant to address the problems mentioned in the paragraphs above. In our design, all the wetted surfaces are either 316 stainless steel or nickel. The system was designed to operate down to liquid nitrogen temperature and up to 7 MPa pressure. A cryopumping technique used to transfer a purified sample to an all-metal storage vessel is also described.

2. Experimental

2.1. Gas chromatograph

Our prep-GC system was based on a Model PSGC-10/40 automated instrument made by Varex[1] (Burtonsville, MD, USA). The complete system as used in our laboratory is diagrammed in Fig. 1. The manufacturer provided the computer, printer, interface, GC control unit, oven assembly, part of the sample inlet system, and a custom-made fraction collection system built to our specifications. The GC control unit regulated the carrier gas flow-rate, oven and vaporizer temperatures, sample injection, and fraction collection. The control unit also monitored the

[1] Mention of manufacturers and brand names is to provide a complete description of the apparatus and does not imply endorsement by the National Institute of Standards and Technology or that the items are the best available for their purpose.

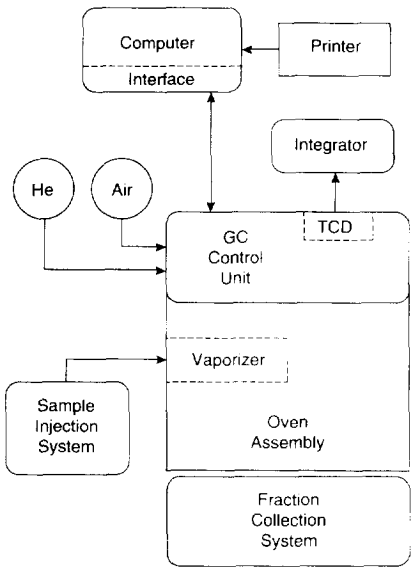

Fig. 1. Block diagram of the preparative-scale GC system used in our separations.

system for alarm conditions and would place the instrument in a safe configuration in case of a failure such as loss of carrier gas flow. A thermal conductivity detection (TCD) system monitored the evolution of gas through the column. An integrator (Hewlett-Packard Model HP3390A, Rockville, MD, USA) was used to record the TCD output and to integrate peaks. Helium (99% assay) was used as the carrier gas while compressed air was used to operate the pneumatic valves.

The prep-GC unit was capable of either manual control from the GC control unit front panel or of automatic control by the computer. The sample injector, fraction collection valves, and oven and vaporizer temperatures were computer controlled for unattended repetitive separations. Software developed by Varex provided for keyboard entry and hard disk storage/retrieval of the process control parameters and runs under MS-DOS (Microsoft, Redmond, VA, USA).

2.2. Sample inlet system

The system provided for both manual and automatic sample injection into the vaporizer. Samples could be manually injected through the injection port septum with a syringe. This technique was sometimes used to find an optimum injection size or to check sample purity during development of a separation protocol.

Samples that were liquids at room temperature were pumped into the vaporizer by an Eldex (Eldex Labs., Napa, CA, USA) precision metering pump. The liquid injection system is shown in Fig. 2. Samples that were sensitive to air were placed in a sealed container and pressurized with an inert atmosphere such as nitrogen or helium. The desired amount of liquid injected into the vaporizer was determined by the pump rate and the injection time. In the automatic mode, the duty cycle for the metering pump was controlled by the computer according to a schedule defined by the user. The pump could also be operated manually. The small-bore capillary tube, used to connect the pump to the vaporizer, added very little dead volume to the injection system; thus, it did not cause significant broadening of the chromatographic peaks. This method did not work for one of our liquid hydrofluorocarbon samples which boiled near room temperature, because the liquid boiled in the pump. Instead, this sample was heated in a bath and injected into the vaporizer as a gas.

Liquefied samples which are normally gases at ambient temperature and pressure were metered through a pneumatic actuated valve. Fig. 3 shows a diagram of the gas injection system. A sample that has a low vapor pressure near room temperature had to be heated until its vapor pressure was well above the column pressure. Then, the difference between the vapor pressure and the column pressure would drive the sample

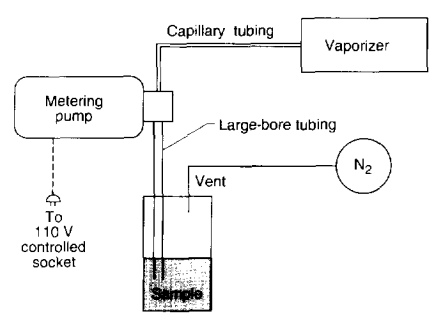

Fig. 2. Liquid sample injection system; schematic diagram.

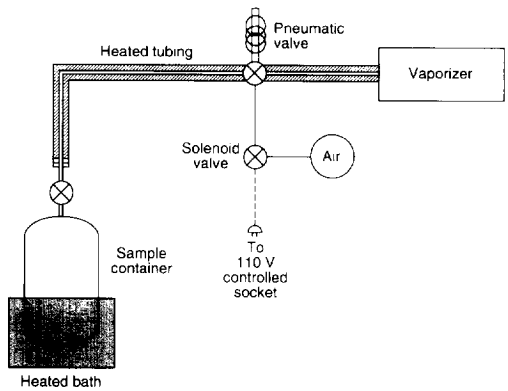

Fig. 3. Gas sample injection system; schematic diagram.

into the vaporizer when the pneumatic valve was opened. The tubing connecting the valve to the sample container and the vaporizer was heated above the bath temperature to prevent condensation in the tube. The preset duty cycle of the valve and the constant vapor pressure of the liquid in the storage container ensured that a reproducible amount of sample was injected. As long as there was liquid in the storage container, the vapor pressure regulated the amount of sample that was forced into the vaporizer.

2.3. Sample collection system

The fraction collection assembly was composed of six sample collection vessels, shown in Fig. 4, which could be selected manually or under computer control. Each port was a modular design consisting of a condenser, valves, and a collection trap. The sections were fastened together with zero clearance, face seal metal gasket connectors (VacuSeal; Parker Hannifin, Huntsville, AL, USA or VCR; Cajon, Macedonia, OH, USA). The prep-GC unit allowed easy access to the sample collection system for modifications. All wetted surfaces of the assembly were made from stainless steel or other non-corrosive metals. There were no elastomer O-rings, grease, or PTFE seals in the collectors or in the valves that were wetted by the sample. The condenser unit was thermostated by a flowing heat transfer fluid, such as tap water or antifreeze solution, from a circulating bath. The

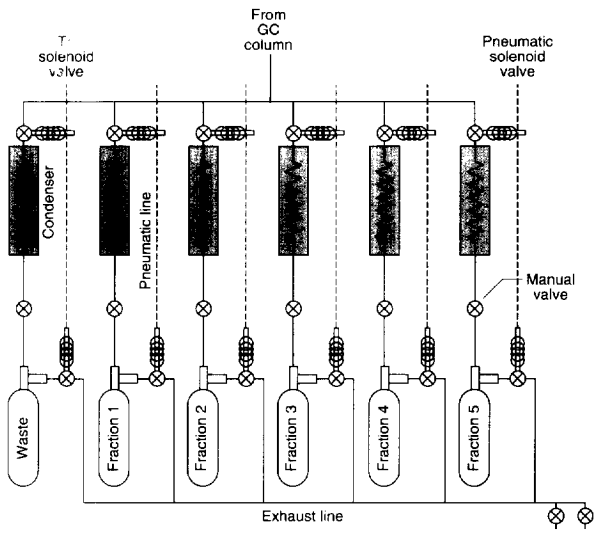

Fig. 4. Schematic diagram of the six fraction collection modules connected as a unit.

all-metal collection trap could be used down to liquid nitrogen temperature and up to 7 MPa pressure.

A normally closed pneumatic valve was located before each condenser and another was located after each fraction collection vessel. Each pair of valves operated in unison to divert the carrier/sample stream through the selected vessel and to prevent contamination from the exhaust line into the chilled collectors. Only one of the fraction collection modules was open at any given time. When desired fractions were not present, the designated waste module was open. The manual valve located between each condenser and its collection module was closed to isolate the fraction collection vessel from the condenser during cryo-transfer procedures.

Fig. 5 shows a cross-section of a fraction collection vessel. The vessel design was similar to a liquid nitrogen trap with a tube extending about a third of the way down the collection vessel. The tube was curved towards the side to allow the carrier gas and sample fraction to impinge on the liquid nitrogen-cooled wall. This configuration was used to improve collection efficiency by capturing aerosols which might otherwise be swept away with the carrier gas. The neck of the collection vessel was heated to

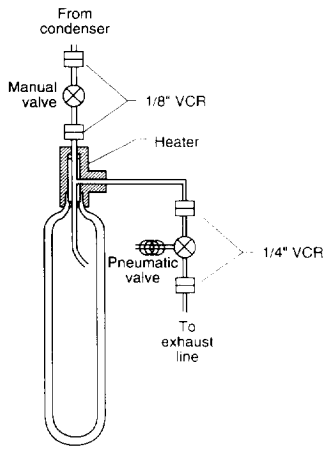

Fig. 5. Cross-sectional view of the fraction collection vessel and associated hardware. 1″ = 1 in. = 2.54 cm.

about 60°C with an electrical heater tape to prevent the incoming sample from freezing there and blocking the flow of carrier gas.

2.4. GC operation sequence

The major components of the carrier gas system are shown in Fig. 6. The sample was injected through the septum or the automatic injection port into the vaporizer where it was vaporized and mixed with pre-heated carrier gas. The carrier/sample mixture then passed through the chromatographic column where separation of the sample into its components took place.

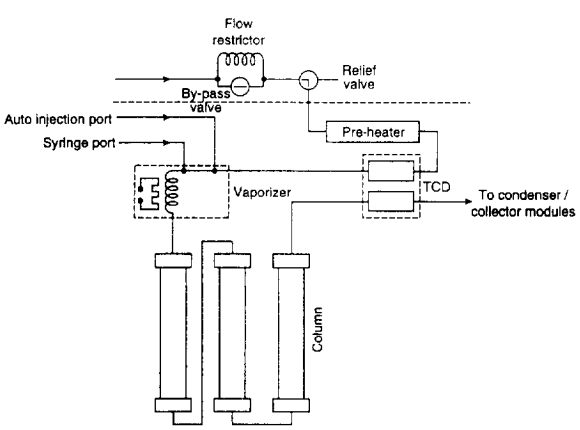

Fig. 6. Schematic diagram of the prep-GC carrier gas flow system (by permission of Varex).

Separated fractions passed through the TCD system and finally through the selected condenser/collection module. Samples were injected into the vaporizer under low carrier gas flow conditions by opening a by-pass valve to force the carrier gas through a flow restrictor. A relief valve was then momentarily opened to rapidly decrease the pressure in the vaporizer just before injection of gas sample. After the injection period, the by-pass valve was closed and the carrier gas flow was returned to its normal level. This procedure concentrated the sample at the head of the column.

TCD was used to monitor the degree of peak separation during the development of a separation process. When the system was performing repeated injections under computer control, TCD was turned off, and all events (injection, fraction selection, cycle completion) were based on time alone. The system conditions and the sample injections were very reproducible from cycle to cycle.

2.5. Sample transfer

Samples were transferred from the collection vessels to the sample storage containers by cryopumping. Fig. 7 shows the components used

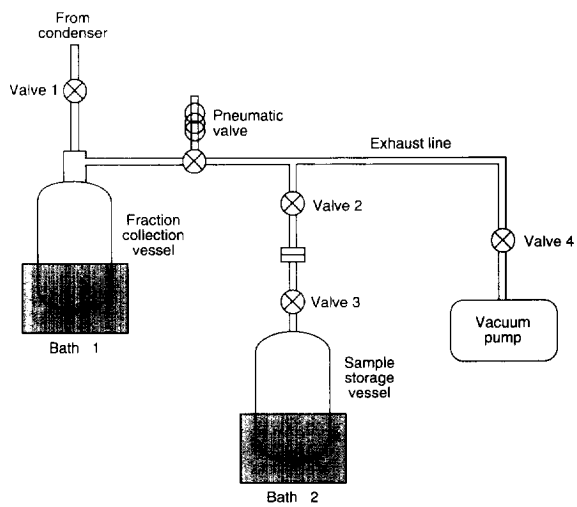

Fig. 7. Schematic diagram of the fraction collection plumbing used during cryopumping procedures. Irrelevant parts of the apparatus have been omitted for clarity.

during cryo-transfer procedures after a separation was completed. First, bath 1 was filled with liquid nitrogen, then the fraction collection vessel containing the frozen sample was isolated from the condenser by closing the manual valve 1. Next, the carrier and residual gases were pumped away through the pneumatic valve and valves 2, 3 and 4 with the attached mechanical vacuum pump. For the final step, valve 4 to the vacuum pump was closed. Bath 2 was then filled with liquid nitrogen, and bath 1 was emptied. The difference between the vapor pressures of the sample in the collection vessel and in the storage vessel drove a mass flow of the sample, and as the collection vessel was warmed this flow was toward the storage vessel. The warming rate and the temperature of the collection vessel were determined by observing the boil-off of the liquid nitrogen in bath 2 as the sample condensed in the storage vessel. The fraction collection vessel was slowly heated with a warm heat gun (or by filling bath 1 with warm tap water) until a steady, smooth boiling was achieved. When the nitrogen stopped boiling, the transfer was complete. Manual valves 2 and 3 were closed, and the purified sample was removed. The entire sample transfer procedure took approximately 10 min.

The sample storage vessels were designed to keep the purified material clean. They were single-ended, stainless-steel cylinders with a welded bellows cut-off valve leading to a high-vacuum fitting that was used to connect the vessel to other apparatuses. All joints were heliarc welded, and the container was tested under vacuum for leaks. The only opening to the purified sample was through manual valve 3.

3. Results

The performance of our prep-GC system is illustrated by the purification of pentafluoroethane. GC analysis before and after purification was performed using an analytical chromatograph with an automatic gas injector valve, a 60–80 mesh Carbopack B/5% Fluorcol

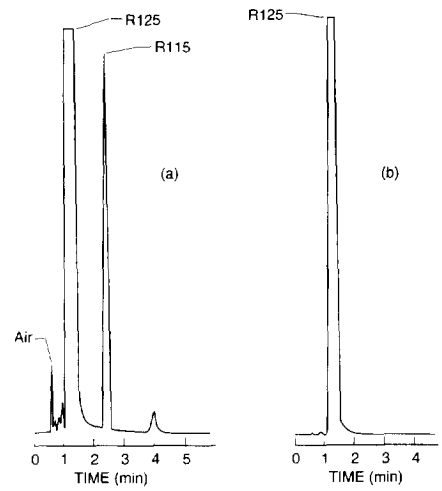

Fig. 8. Analytical chromatograms of the (a) as-received and (b) purified samples.

(Supelco, Bellefonte, PA, USA) packed column, 3 m × 3 mm O.D., and a TCD system. The temperature of the column was kept isothermal at 45°C. The carrier was helium gas at a nominal flow-rate of 50 ml/min. A chromatogram of the as-received sample of pentafluoroethane, R125, is shown in Fig. 8a. The peak areas from the analysis are given in Table 1. The chromatograph was calibrated using a gravimetrically prepared mixture of R125 and R115. The results showed that the sample contained 0.0015 ± 0.00007 mole fraction R115.

Table 1
GC analysis of as-received pentafluoroethane

Retention time (min)	Fraction area (%) (± 0.005)	Compound
0.64	0.030	Air
0.76	0.002	Unknown
0.89	0.005	Unknown
0.97	0.006	Unknown
1.10	99.697	Pentafluoroethane (R125)
2.42	0.241	Chloropentafluoroethane (R115)
3.98	0.019	Unknown

The as-received sample of R125 was processed through the preparative system using the gas injection system (Fig. 3). The same packing material used for the analytical work, namely 60–80 mesh Carbopack B/5% Fluorcol, was packed into a 2 m × 1 cm I.D. column and installed into the prep-GC system. The column temperature was isothermal at 45°C, while the vaporizer and detector were maintained at 60°C. The carrier gas was helium with a flow-rate of 400 ml/min. The helium carrier gas was easily removed from the purified sample by repeated freeze–pump–thaw cycles. The fraction collection vessel was immersed in a liquid nitrogen bath. The neck of the fraction collection vessel was heated to prevent freezing of the sample in the small-bore inlet tube, as discussed previously. The coiled condensers were not required for this separation and the jacket bath contained only air.

During each cycle, the automatic valves were programmed to divert the process stream to the collection cold trap just after the start of the R125 peak. Shortly before the end of this peak, the valves sealed off the collection trap and returned the stream to the normal pattern. Each cycle took 6 min to complete. After 17 cycles, a total of 7.65 g of R125 had been collected for a process rate of 4.5 g/h. The collected mass represented an estimated 80–90% of the injected sample. The purified R125 was then transferred to a sample storage vessel for analysis, using the cryopumping technique described earlier.

A chromatogram of the purified R125 is shown in Fig. 8b and the peak analysis is given in Table 2. The conditions for this analysis were identical to the analysis of the as-received sample. Within the resolution of the instrument, all of the main impurities had been successfully removed.

Table 2
GC analysis of purified pentafluoroethane

Retention time (min)	Fraction area (%) (±0.005)	Compound
0.92	0.007	Unknown
1.19	99.993	Pentafluoroethane (R125)

4. Discussion

Safety issues were a concern in the design of this system. Many hydrofluorocarbons are stored as liquified gases with very high vapor pressures at room temperature. The all-metal system described here was capable of containing the purified sample in case of system failure and loss of liquid nitrogen in the fraction collection bath. Cryogenic fluids in the baths could be maintained overnight by a liquid nitrogen level control system. The worst-case scenario expected would be the thawing of the purified sample and the opening of the pneumatic valve by the high vapor pressure followed by loss of the purified sample. The pneumatic valves were normally closed by spring tension and opened by compressed air and were susceptible to being forced open by high sample pressure. In the event of a power failure, the oven and vaporizer temperature controllers would be disabled, the pneumatic valves to the collectors would close, and the carrier stream would be diverted through the normally open valve to the waste module. Normal operation could not resume until the system was manually reset.

The sample collection system was cleaned before use by heating and flowing carrier gas through it or evacuating it with a vacuum pump. We did not find any contamination problems with the purified fractions associated with the use of research-grade helium as a carrier gas. In the event that such contamination occurs, liquid nitrogen-cooled molecular sieve traps would be used to clean the carrier gas. The design of the fraction collection and storage vessels allowed the purified samples to be transferred to our experiments without ever being exposed to air or other unwanted materials.

We have described a new all-metal collection system for a preparative gas chromatograph that will operate down to liquid nitrogen temperature

and pressures up to 7 MPa. The performance of the system was demonstrated through the purification of a pentafluoroethane–chloropentafluoroethane (99.85:0.15) mixture to achieve 99.99% pentafluoroethane at a rate of 4.5 g/h.

Acknowledgement

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