

retention time vs. temperature plots, indicate that while solubilities would be smaller, separations would be increased by operation at a slightly higher temperature. The linear flow rate through this column at 90 atm ethane is observed to be 7 cm/s—slightly slower than the optimum 20 cm/s for a standard capillary column and within the range of acceptable values.

The major problem encountered thus far has been plugging of the nozzle orifice caused both by foreign particles and by sample deposition. Even with carefully filtered (multiple-stage, 5 μm) solvent gas and a dual 5/2 μm filter placed directly between the final zero-dead-volume shut-off valve and the nozzle orifice, we have observed slow closure (after 1 to 10 h of operation) of the nozzle orifice from particle accumulation correlated with actuation of the preceding valve, the packing of which is graphite-filled fluorocarbon polymer. Inspection of the orifice once showed a symmetrical black deposit about the entire circumference with a long, thin particle ($\sim 2 \mu\text{m}$ by $15 \mu\text{m}$) centered along a diameter. Installation of a triple 2./0.5/0.5 μm filter appears to have eliminated particulate buildup.

A particulate plug could be dislodged only by removing the nozzle assembly from the system, whereas a solute plug of the compounds studied could be removed by alternately evacuating and pressurizing from the upstream side of the orifice and/or rapid heating of the nozzle tip. The nozzle tip was usually operated at bath temperature because heating a dense gas which is essentially at the critical point decreases its solvent power with resulting deposition of solute. We have also seen solute deposited on the vacuum side of the orifice in such a way that it deflects gas flow from the beam center-line instead of stopping it.

At this point our test quantities (0.03 mg to 0.3 mg) of different solutes appear to have been too large to maintain an open orifice. There was typically plugging or partial plugging. The partial plugging was detected by lowered solvent gas intensity, increase in skimmer mid-point temperature, lowered expansion chamber pressure, and quite often an increase in solvent gas polymers. With a pure gas beam, a thermocouple mounted at the mid-point of the beryllium copper skimmer gave a temperature reading 20–30 $^{\circ}\text{C}$ lower than one on the skimmer base ($\sim 6\text{-mm}$ separation). Upon sample elution the mid-point temperature at times dropped erratically to as low as -35°C with the base temperature close to $+30^{\circ}\text{C}$. With visual inspection through a viewing port, we have seen neither deposits on the skimmer nor aggregates in the beam even at the very low skimmer temperatures.

While we have seen some clustering of solute with solvent gas— $(\text{C}_6\text{H}_6)(\text{CO}_2)$, $(\text{C}_6\text{H}_6)(\text{CO}_2)_2$, $(\text{C}_{10}\text{H}_8)(\text{C}_2\text{H}_4)$, $(\text{C}_{10}\text{H}_8)(\text{C}_2\text{H}_4)_3$ with the cluster intensity less than 20% of the solute intensity; it has not been seen with the larger, less volatile molecules

and the higher solvent gas densities required to elute them.

There appears to be a definite effect of solute upon solvent cluster formation, in that cluster formation often is inhibited by the presence of solute. This is reasonable in view of the greater number of collisions in the beam when species of greatly different molecular weight are present. Neither these collisions nor those with background gas which also break up solvent clusters seem to have major effect on the heavier solute molecules in the molecular beam over the limited pressure range of our studies to date. In fact, it appears that by proper adjustment of background gas pressure the weakly bonded solvent- and solute-solvent complexes may be destroyed with resultant simplification of the higher molecular weight spectrum to that of solute molecules only.

While it is clear that further refinements and studies are needed, e.g., small volume sample introduction system, solvent gas and column selection, solvent gas density programming, use of mixed solvent gases, beam enrichment measurements, etc., the preliminary results indicate that a molecular beam interface between a dense gas chromatograph and a mass spectrometer is quite practicable and should have many applications.

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Calibration and Performance of a Thermal Converter in Continuous Atmospheric Monitoring of Ammonia

Sir: The important nitrogen-containing compounds in the atmosphere are N_2O , NO , NO_2 , and NH_3 , and salts of NO_2^- , NO_3^- , and NH_4^+ . The oxides of nitrogen (NO_x), namely, nitric oxide (NO) and nitrogen dioxide (NO_2), are significant atmospheric pollutants. Although primarily emitted by natural sources, ammonia (NH_3) from anthropogenic emissions contributes significantly to local concentrations.

Atmospheric NH_3 results naturally from biological decay at the Earth's surface. The following processes account for

the fate of NH_3 in the atmosphere (1): (1) Absorption on wet surfaces to form NH_4^+ , (2) Reaction with acidic material in either gaseous or condensed phases to form NH_4^+ , and (3) Oxidation to NO_2^- . Routes 1 and 2 account for the fate of approximately 75% of the NH_3 , and Route 3 for the remaining 25% (1).

Wet chemical methods for determination of ammonia (e.g., Nesslerization) are tedious and not easily adapted to on-line monitoring of emissions. The efficiency of ammonia uptake

Table I. NH_3 Permeation Rates for Permeation Tubes at $30.0 \pm 0.5^\circ\text{C}^a$

low permeation device	19.8 ± 1.5 ng/min
2-cm std permeation tube	656.2 ± 27.4 ng/min
4-cm std permeation tube	1299.0 ± 72.4 ng/min

^a Statistical analysis based on 95% confidence interval.

in the liquid phase for concentrations $<20 \mu\text{g/L}$ (NH_3 -nitrogen) is also unreliable (2). Current chromatographic methods require a high NH_3 concentration (>500 ppm). Other instrumental methods (e.g., electrochemical) are either too slow in response time to be applicable to real-time monitoring or else very expensive.

METHODS

Known concentrations of ammonia were obtained from permeation tubes (3). The NH_3 Dynacal permeation tubes (commercially prepared) were calibrated at 30.0°C by the weight loss technique. A stable temperature ($\pm 0.5^\circ\text{C}$) was maintained with a constant temperature water bath. The system adapted for this purpose was as recommended by the manufacturer (4). Gaseous nitrogen, from a cylinder, was used to flush ammonia from around the permeation tubes. Statistical analyses on the weight loss vs. time data were performed with a computer routine and the permeation rates ascertained on a 95% confidence limit.

Different NH_3 permeation tubes were used to generate various levels of NH_3 . Table I gives a comparison of the permeation rates. The gas flow meters (rotameters) were calibrated prior to the commencement of the experiment with a soap bubble method.

The heart of the NH_3 converter is a coil constructed from 1.829 m of Type 316 stainless steel tubing (0.318-cm o.d., 0.071-cm wall thickness). The tubing is coiled to approximately 5 cm in diameter, sheathed in Refrasil tubing, and wrapped with heat-resistant tape. Stainless fittings are attached to each end of the coil, and a Chromel-Alumel thermocouple (0 – 1000°C) is attached to the midpoint of the coil. The coil is then placed in a metal container which is insulated with aluminum foil and Fiberfron. The coil is electrically insulated from the container by Teflon spacers. Heat radiators are attached to the ends of the coil protruding from the container to dissipate axial heat generated within the coil and to provide for electrical connection with a transformer.

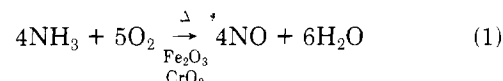
The converter transformer takes the line voltage, usually 115 volts ac, and drops it to approximately 5 volts ac. This low voltage, high current source provides the heating power to maintain the temperature within the coil. The converter temperature controller is an on-off type (Thermo Electron AP1 Model 232). It is connected to the primary (115 V) voltage of the transformer and maintains the set point temperature to approximately $\pm 2^\circ\text{C}$. It is equipped with a fail-safe mechanism that turns off the power if the thermocouple is damaged.

EXPERIMENTAL

A flow diagram for the NH_3 converter calibration system is shown in Figure 1. Nitrogen picks up the NH_3 emitted from a permeation tube at 30.0°C , and the combined gases are mixed with a stream of purified dry air. Since the air flow is in large excess relative to the nitrogen flow, the gaseous composition approximates that in the atmosphere. With this gas dilution system, it was possible, with the lowest permeation device, to generate concentrations of 1 ppb with a precision of 10%. The gases are injected into the ammonia converter where the NH_3 is catalytically converted to NO at temperatures in excess of 800°C on the stainless steel converter. The gases then enter a chemiluminescent nitrogen oxides analyzer. Pure dry air, for cleaning the NH_3 converter, can be injected via a three-port valve interrupting the ammonia flow.

To minimize adsorption effects, the gases come into contact with only Teflon and Pyrex surfaces until they enter the analyzer. The gas flow rates are monitored by rotameters, and temperatures are measured by mercury-in-glass thermometers.

The thermal converter oxidizes NH_3 to NO by the following reaction (5–8):



As pointed out by Sigsby et al. (7), NH_3 response can be segregated from the NO_x response by a subtractive method.

RESULTS AND DISCUSSION

The ammonia converter was calibrated at 700, 800, and 900°C for a fixed sample flow rate of 400 mL/min, and the calibration curves are presented in Figures 2 and 3. These curves indicate that above 800°C , the conversion of NH_3 to NO is the same at both 800°C and 900°C (Figure 2). The efficiency of the converter at 800°C is greater than that at 700°C , as seen from the slopes in Figure 3. Sigsby et al. (7)

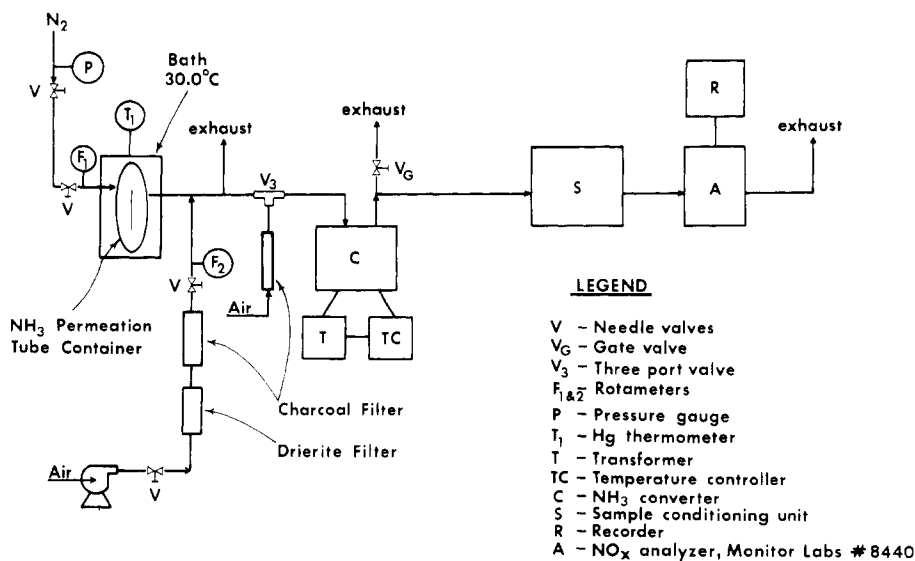


Figure 1. Ammonia converter calibration system

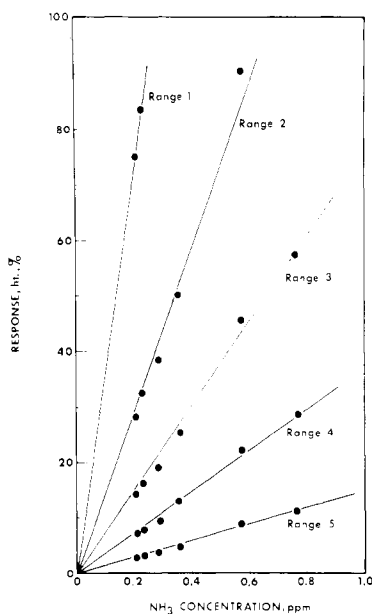


Figure 2. Ammonia converter calibration at 800 °C and 900 °C

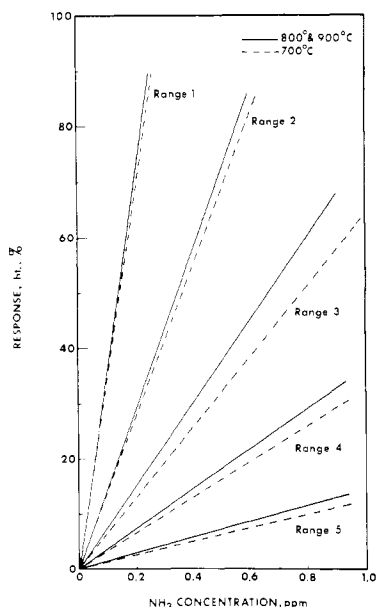


Figure 3. Comparison of ammonia converter calibration at 700, 800, and 900 °C

reached similar conclusions, pointing out that depending upon sample flow, when a 1.829-m converter tube is utilized, temperatures between 750 and 900 °C are required.

The source of zero air was ambient air filtered by activated carbon and dried by Drierite (Figure 1). The zero line was established with this air. The zero line was checked before, after, and periodically during the experiment. The activated carbon and Drierite were changed periodically (~6 h of operation).

The efficiency of conversion of NH_3 to NO of the NH_3 converter at 800 °C was determined with a known source of NO. Within the precision of the technique, it was found to be 100%. The NO concentration was determined before the efficiency measurement by standard techniques. The source of NO was a high purity cylinder gas (Matheson Gas Products).

The NH_3 source was a calibrated NH_3 permeation tube. Table II gives analyses for NH_3 converter efficiency measurements.

This method permits continuous monitoring of NH_3 over

Table II. NH_3 Converter Efficiency Measurement at 800 °C

permeation rate of NH_3 = 1299 ng/min at 30.0 ± 0.5 °C permeation tube

analysis of NO (in N_2) gas cylinder NO 50.1 ppm
(performed by Research Triangle Institute, RTP, N.C.) NO₂ 1.7 ppm
temperature of NH_3 converter 800 °C

sample no.	range of analyzer	NH_3		NO		efficiency (%) [95% C.I.]
		concn to analyzer, ppm	response, %	concn to analyzer, ppm	response, %	
1	4	0.55	20	0.55	19	105 ± 5
2	4	1.6	56	1.6	56	100 ± 5

a range of concentrations (>5 ppb). The response is linear. The response time is less than 2 min and is primarily a function of the conditioning of the converter with NH_3 ; here a period of 12 h was used. The system described provides a convenient, steady, and rapid analysis of NH_3 in the gas phase at heretofore impossibly low concentrations. It is important to recognize that NO and NO₂ as well as other nitrogenous compounds such as amines, etc., are potential interferences, requiring that NH_3 be obtained by a subtractive technique in such instances. This instrumentation functioned well in studying NH_3 uptake by selected plant species (9).

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AIDS FOR ANALYTICAL CHEMISTS

Removal of Excess Chelating Reagent Prior to Gas-Liquid Chromatography of Chelated Chromium

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Gas-liquid chromatography (GLC) of β -diketone chelates has been shown to be a very sensitive procedure for the analysis of certain trace metals. While a number of β -diketones form volatile metal chelates suitable for gas chromatographic analysis, the majority of practical applications of this technique involve the use of 1,1,1-trifluoro-2,4-pentanedione ($H(tfa)$) as the chelating reagent. This reagent has been used by Taylor et al. (1) and Taylor and Arnold (2) to prepare beryllium chelates, by Hansen et al. (3) and Black and Sievers (4) to prepare chromium chelates, and by Wolf et al. (5) for both beryllium and chromium. Quantitative analyses of these metal chelates utilizing electron capture, mass spectrometric, and microwave emission detectors have been reported. While these detectors vary greatly in characteristics, they are all hampered by the presence of the large amounts of unreacted chelating reagent ($H(tfa)$) found in chelation reaction mixtures. To remove this source of interference, researchers have relied on a base extraction procedure whereby the residual ($H(tfa)$) is converted to $(tfa)^-$ and extracted into the aqueous phase prior to chromatography of the organic phase which contains the metal chelates. Because this technique suffers from irreproducible removal of $H(tfa)$, possible degradation of metal chelates, and multiple transfers, we have investigated alternative means of $H(tfa)$ removal from samples to be analyzed for chromium content by GLC. We have found that the use of small glass columns filled with the ion-exchange resin, Chelex-100, is an effective means of accomplishing this, at least in the case of chromium trifluoroacetylacetonate chelates.

EXPERIMENTAL

Glass columns of dimensions, 5×110 mm with a 4-mL top reservoir and fritted glass end plate, were fabricated in-house.

They were prepared for use by slurring approximately 1 g of Chelex-100 ion-exchange resin (200-400 mesh) (BioRad, Richmond, Calif.), in 0.1 N KOH, and filled by gravity flow. After filling, they were washed with an additional 20 mL of 0.1 N KOH and then aspirated from the bottom employing vacuum from a water aspirator. Hexane (J. T. Baker analyzed reagent grade) was aspirated through the columns until a flow of 0.5-1.0 mL/min was established. The hexane flow rate obtainable varied depending upon the batch number of Chelex-100 used. When resin manufactured prior to 1974 (batch 12670) was employed, a flow by gravity of 0.5-1.0 mL/min was possible. However, when recently manufactured resin was used (batch 15904), a vacuum assistance device was necessary to obtain this same flow rate (Figure 1). The use of coarser resin (50-100 mesh) to obtain a higher flow is not recommended because of a significant reduction in efficiency of $H(tfa)$ removal. Care should be taken to establish

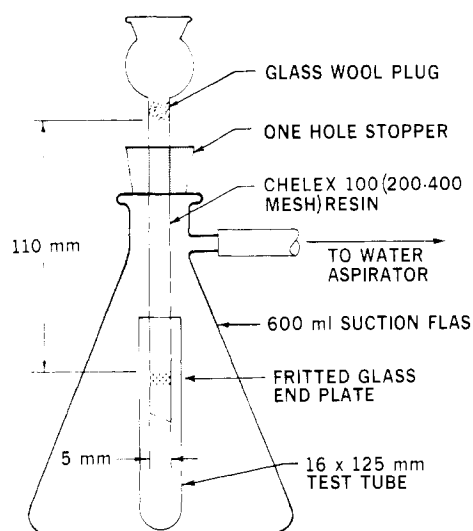


Figure 1. Chelex-100 resin column for removal of $H(tfa)$ and suction apparatus for increasing and stabilizing hexane flow rate

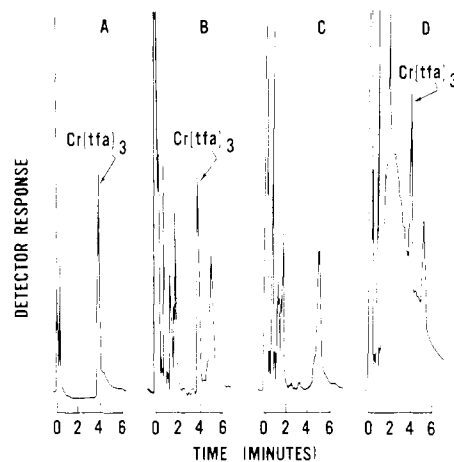


Figure 2. Chromatograms of (A) pure $Cr(tfa)_3$, (B) and (C) extracts of chelation reaction mixtures processed on Chelex-100 columns and (D), base washed reaction mixture extract. GLC column = 2.0 M \times 2.0 mm i.d. glass, packed with 3% OV-1 on 80/100 mesh Supelcoport, column oven temperature = 135 $^{\circ}C$, N_2 flow = 40 mL/min. ^{63}Ni electron capture detection

an adequate, constant flow of hexane prior to adding the sample.