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# METHODS OF CHEMICAL ANALYSIS FOR OIL SHALE WASTES

by

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ABSTRACT

This report describes methods of chemical analysis which are necessary in order to adequately test the various pollution control technologies which are presently being proposed for the treatment of oil shale retort gases and wastewaters. It includes step-by-step protocols for determining important species and it provides supporting evidence and discussion to allow the analyst to adjust the procedure to the varied sample types which he may encounter. Emphasis is placed on methods which are sufficiently rugged and rapid to be useful on site during the field testing of pollution control systems.

A type of ion exchange chromatography, referred to in the literature as suppressed ion chromatography, has been applied for the determination of major and minor anions in retort wastewaters. Original experience with this method for retort wastewaters indicated the presence of very late-eluting compounds which could not be removed from the column in a reasonable time and which would interfere with subsequent analyses. This problem was solved with a column switching arrangement which allows the late eluters to be separated on a pre-column while the earlier-eluting compounds are separated on the main analytical column. The same valve and column configuration can be used for four different protocols: the first protocol, referred to as the majors protocol, determines $SO_4^{=}$, $NO_3^-$, $S_2O_3^{=}$, and $SCN^-$ in a single run using 7 mM $Na_2CO_3$ as an eluent. The second protocol determines the late eluters, $S_2O_3^{=}$ and $SCN^-$ using an eluent of 7 mM $NaCO_3$ + 0.5 mg/l of $SCN^-$. Earlier eluters are determined by the third protocol using a valve switching arrangement which traps the late eluters on a pre-column, which is periodically flushed to waste. Peaks which can be observed with this procedure include $Cl^-$, acetate, $NO_2^-$, $SO_3^{=}$, $NO_3^-$, $PO_4^{3-}$ and $SO_4^{=}$, although not all have been successfully separated when present in the same solution. While the valving and

column configuration remain unchanged, the analysts must be prepared to adjust the eluent for the various types of samples and analytes encountered. The fourth protocol is for the measurement of total sulfur and is carried out by oxidizing the various sulfur species present to $SO_4^{=}$, which is then determined by the protocol for the early eluters.

The determination of sulfide by potentiometric titration with Pb(II) has been investigated for retort wastewaters. Thiocyanate, thiosulfate, sulfate, chloride, carbonate, ammonia, and hydroxide ions, which are components of retort waters, have been tested as potential interferences for sulfide concentration in the range 1-1,000 mg/l and have been shown to be insignificant within the normal range of interest. The titration has been evaluated under field conditions with actual retort waters with regard to precision, recovery, reliability, and ease of use. The titration procedure has also been compared to the direct calibration method with the AgS ion selective electrode. The titration procedure, which includes an AgS ion selective electrode to monitor the titration and a Gran's plot end point, is the preferred method of analysis.

Thermal evaporation, lyopholization, and the measurement of colligative properties have been investigated as measurements of the total solute content in retort wastewaters. Of these, both thermal evaporation and lyopholization were shown to be inappropriate. Of the various colligative properties considered, the freezing point depression was shown to be the best measurement of total dissolved solutes. Using this method the total solute content can be measured in units of moles/liter over the range 0.001 - 3.0 moles/liter (counting each ion separately).

Three distinct methods have been developed for the analysis of ammoniacal N in retort waters. The first method uses an ammonia selective electrode but

minimizes many of the problems associated with this device by maintaining the electrode in pure standard to which small amounts of sample are added. The second method, ion chromatography, separates $NH_4^+$ on an ion exchange column with detection by electrical conductivity. The third method involves absorption of UV radiation by ammonia in the headspace over a basic sample solution. All three methods are capable of quantitating ammoniacal N in turbid, briny, and organic-laden wastewaters but are distinguished by several secondary characteristics. For example, the first method requires the least investment in equipment but is the most labor intensive and least precise. The ion chromatographic method is readily implemented with commercially available equipment and also is capable of measuring Na and K simultaneously. The gas absorption method is promising as the basis for an on-line, unattended monitor and is capable of distinguishing between aqueous $NH_3$ and $NH_4^+$. It is the most precise measurement but requires spectral background correction in order to achieve accurate results.

A method for measuring total sulfur in oil shale retort gas is described. The method operates by converting the various sulfur species to $SO_2$ which is then monitored by a commercially available monitor. Two devices, a heated tube and a flame, have been evaluated for converting the various individual sulfur species to $SO_2$. Of these, the conversion efficiency in the tube was shown to depend both on the temperature and the species being oxidized, undesirable performance for this purpose. The flame was shown to convert essentially 100% of the various sulfur species to $SO_2$. Based on this performance, a device was constructed for the measurement of total sulfur in retort gas and tested at an oil shale retort. The total sulfur measured with the flame converter agreed within experimental error with the sum of the individual sulfur species.

Gas chromatography with flame photometric detection was developed as a means of measuring sulfur species in retort gas. Two potential problems were considered in detail in order to establish the veracity of this technique: First, hydrocarbons, one of the major components of retort gas, are known to quench the fluorescence of the flame photometric detector (FPD), and it was necessary to determine whether this would be a problem in realistic retort gas. The second potential problem was the large number of sulfur species which could occur in retort gas. Without prior knowledge one can easily number twenty possible gases, which thus must be separated from each other if an unambiguous assignment is to be made to each.

Fluorescent quenching effects were measured on two types of commercially available FPD's, a single-flame detector and a dual-flame detector. The latter exhibited no significant quenching effects over the concentration ranges of interest in retort gas. However, for the single flame detector quenching effects cannot be ruled out entirely. Although hydrogen sulfide in retort gas is usually abundant enough to minimize quenching effects, the minor species could be subject to quenching effects unless precautions are taken. These precautions include operating the detector with the air and hydrogen flows reversed and measuring peak height rather than peak area. In addition, columns are selected that minimize co-elution with hydrocarbons. The single flame detector exhibited both suppression and enhancement of the fluorescent signal.

Because of the large number of sulfur species which could conceivably occur in retort gas, it became apparent that a single packed column could not unambiguously separate all possible species. Efforts were therefore made to find a column which would separate the compounds of primary interest--hydrogen sulfide, carbonyl sulfide, sulfur dioxide, carbon disulfide, methyl mercaptan, and ethyl mercaptan--from each other as well as from the later eluting sulfur

compounds. Several columns were evaluated with regard to their ability to achieve this separation as well as the required separation from hydrocarbons. Columns were also tested for their ability to tolerate water vapor as well as the other compounds in retort gas. The best general purpose column packing for the determination of the sulfur compounds of primary interest was a Carbopack B HT 100, although a Chromosil 310 packing would be useful for the occassional determination of thiophenes. A protocol for the primary sulfur species is described for the concentration range of 5-50,000 ppmv using a Carbopack B HT 100 column arranged in a backflush-to-detector configuration.

Electrical conductivity, pH, alkalinity, and total inorganic carbon, while not investigated explicitly in this study, are discussed briefly. It is suggested that the measurement of pH and electrical conductivity with the standard conductivity cell and pH electrode, respectively, has demonstrated no obvious problems, although frequent cleaning and calibration should be expected. It is recommended that the alkalinity test be discontinued as a measurement of dissolved carbon dioxide because of interferences due to ammonia and organic acids. Dissolved carbon dioxide should instead be determined by commercially available analyzers which are also suitable for total organic carbon measurements. Precautions for the latter two measurements are discussed in the text.

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# SECTION 1

# INTRODUCTION

This report is written for chemists and engineers who are responsible for developing pollution control technology for the oil shale and related synthetic fuels industry. It describes several methods of chemical analysis which are necessary in order to adequately test the various pollution control technologies which are presently being proposed for the treatment of oil shale retort gases and wastewaters. When possible, it includes step-by-step protocols for determining important species, and in every case, it provides supporting evidence and discussion to allow the analyst to adjust the procedure to the varied sample types which he may encounter.

It has been recognized for some time that many methods of chemical analysis which are appropriate for relatively simple stack gases and wastewaters are not appropriate for retort gases and wastewaters (Fox et al., 1978; Felix et al., 1977; Farrier et al., 1977; Wildeman and Meglen, 1979; Wildeman, 1979; Wallace, 1981). This situation arises largely because of the large number of interfering materials found in many retort samples for which the standard methods are not designed. For this reason, the U.S. Environmental Protection Agency initiated an effort to develop improved methods of chemical analysis for oil shale wastes. This effort is summarized in this and a previous report (Wallace, 1981).

The objective of the work described in this report is to develop methods of analysis which are helpful in selecting, monitoring and optimizing the various pollution control systems which may be applied to oil shale processes. In the case of wastewaters, present development plans call for "zero discharge" of any contaminated water. The wastewater engineer, therefore, is concerned

with treating the wastewaters for internal re-use and requires analytical methods appropriate for this goal. This means that most methods must be designed for the major and minor components (e.g. ammonia, thiosulfate, etc.) and not necessarily for the same species which are normally of interest to the regulator who is concerned with discharged waters. Retort gases, which are a valuable by-product of the retorting process, represent a similar situation. Such gases will either be burned for heat or otherwise consumed. Once the gas is burned, the resulting flue gas would be similar to flue gases from any number of other utility and industrial sources and should not present special problems to the analyst. However, many development plans call for treating the gas for sulfur and possibly ammonia removal prior to combustion. This requires that the retort gas be analyzed, especially for the various sulfur species which may be present. The measurement of sulfur species is thus one of the procedures described in this report.

These objectives imply that the analytical methods which are developed meet certain criteria. Methods for retort wastewaters must work well with waters which are briney, turbid, colored and which contain high levels of organic oils and solutes. Methods for retort gases must tolerate complex mixtures of hydrocarbons, inert gases, water vapor, and entrained material. In addition, the methods must be sufficiently rugged to operate in a field laboratory where the environmental conditions are less-than-ideal. The analyses described in this report are therefore designed to be used in a field laboratory to provide rapid feedback to the plant operator to optimize system performance. On the other hand, methods designed for these objectives are not necessarily required to be as sensitive as methods designed for monitoring the ambient environment or discharged streams.

Most methods discussed in this report have been applied under field conditions to a limited number of sample types with satisfactory results. For example, application of the methods described to a series of retort wastewaters herein resulted in satisfactory ion balances. At this stage it is prudent to test these methods with a wider variety of waters and gases, an activity in which the authors are presently engaged. The authors would also welcome comments from other analysts regarding their experience with the methods described in this report. It is hoped that these methods will be applicable not only to oil shale retort process streams, but also to synfuel wastes generally.

The recommended methods of analysis are summarized in the final chapter of this report. For information on additional methods, especially trace elements, the reader is referred to the first report prepared in this project (Wallace, 1981).

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## SECTION 2

## MINOR ANIONS IN RETORT WASTEWATER BY ION CHROMATOGRAPHY

Previous investigators have shown that, in addition to $HCO_3^-$ and $CO_3^=$, several important minor anions also occur in retort wastewaters. For example, Haas (1980) reported sulfide in the range of 500-1,000 mg/l as the major anion after $HCO_3^-$ and $CO_3^=$ in condensate from the TOSCO II process. He also reported total organic acids at levels of approximately 4,000 mg/l. On the other hand, Fox et al. (1978) reported an absence of sulfide but the presence of the more oxidized sulfur species $S_2O_3^=$, $SO_4^=$, and $SCN^-$ in a retort wastewater from an in-situ process. Fox's results for $SO_3^=$ were uncertain, ranging from <20 to 925 mg/l, due to the lack of adequate analytical techniques, while a single, unconfirmed determination of $S_4O_6^=$ gave a level of 280 mg/l. On the other hand, Stuber et al. (1978) reported $S_4O_6^=$ to be absent from most retort waters (e.g., <5 mg/l). They also reported the major S species to be $S_2O_3^=$, $SO_4^=$, and $SCN^-$.

Previous work also has suggested the absence of several species. For example, none of the investigators cited in the previous paragraph have detected $CN^-$, $NO_2^-$, $NO_3^-$, or $PO_4^{3-}$ in retort wastewaters, species whose presence might be suspected in the condensate from a combustion source. It has also been proposed that even if $CN^-$ were initially present, it would be removed rapidly by reaction with $S_2O_3^=$ to form $SCN^-$ + $SO_3^{2-}$ (Luthy et al., 1977). While Fox reported significant levels of $Cl^-$, most other investigators report $Cl^-$ only at trace levels; it is thus likely that the $Cl^-$ in Fox's samples was due to the intrusion of ground water which was known to have occurred with these samples. In the authors' experience, largely with retort wastewaters from the 150-ton retort at the DOE facility in Laramie, the prevalent inorganic

minor anions are $S_2O_3^=$, $SO_4^=$, and $SCN^-$. $SO_3^=$ is occasionally observed, for example after waters have been exposed to $H_2S$ and air.

While the above-referenced studies indicate several minor species which occur in retort water, they also indicate a degree of variability among waters from different sources. These investigators, as well as others (Wallace, 1981) also emphasized that many of the analytical techniques were not adequate to determine the desired species unambiguously and quantitatively. This is important because measurement of several of the species discussed above is important to the design and operation of pollution control systems. In addition, if unknown to the analyst, their presence can interfere with other chemical analyses. Their measurement is also important for quality control, since anion/cation balances cannot be completed until their concentrations are known.

The objective of the work described herein was thus to develop reliable methods of chemical analysis for the anions in retort wastewaters. The methods were to be primarily for the purpose of evaluating and controlling the operation of various pollution control systems under field conditions, and as such were to be field-worthy and easily performed by a technician. Results were to be available rapidly in order to aid in adjusting the operation of the pollution control equipment. Another requirement was that the analyses require a minimal amount of equipment and space, so that all necessary supplies and equipment could be easily transported to a field site in a van or small trailer.

The efficacy of both standard and less routine methods for analyzing retort wastewaters has been reviewed by Wallace (1981), to which the reader is referred for more detailed information. Suffice it to say that many methods of analysis clearly needed to be improved or replaced. Others were not suitable

for field use, requiring too much equipment or too much operator time. In many cases, methods were simply not investigated or validated for retort waters in terms of possible interferences, accuracy, or precision.

Because of the necessity of determining several of the minor species in retort water, and because of the inadequacies of the available methods, efforts were made to develop additional techniques for retort water. Ion chromatography (Small et al.; 1975) was selected as a likely technique because of its ability to determine several species simultaneously: it is clearly preferable to field one instrument rather than ten, and more feasible to develop one method rather than several. In this regard, ion chromatography is easily performed in field laboratories, since the instrument is easily transported and minimal supporting apparatus is required.

The application of ion chromatography to complex samples has been described by several authors. For example, Courtney (1976) applied ion chromatography to the measurement of inorganic anions and cations in various biological fluids. Hansen et al. (1979) reported the development of better eluents for the determination of $AsO_4^{3-}$ and $SO_3^{=}$ in leachates from flue dust samples. They also found that $SO_3^{=}$ was difficult to determine by ion chromatography because it readily oxidized during the chromatographic separation. Holcombe et al. (1979) applied ion chromatography to the measurement of $SO_3^{=}$, $SO_4^{=}$, and $S_2O_3^{=}$ in solutions from flue gas desulfurization units. Two separate runs were required, the first with a weaker eluent for $SO_3^{=}$ and $SO_4^{=}$, and the second with a stronger eluent for $S_2O_3^{=}$. McFadden and Garland (1979), in attempting to develop an ion chromatographic method for oil shale wastewaters, succeeded in separating the early eluters $F^-$, $Cl^-$, $NO_2^-$, $PO_4^{3-}$, $SO_3^{=}$, and $SO_4^{=}$ on a single column; the later eluters, $I^-$, $S_2O_3^{=}$, and $SCN^-$ were separated on a different column. Trujillo et al. (1981) measured

$S_2O_3^=$ in leachate from spent oil shale with an ion chromatograph equipped with a shortened column; however, all earlier peaks ($F^-$ to $SO_4^=$) eluted as a single peak. For a more detailed review of the application of ion chromatography to oil shale and other environmental samples, the reader is referred to Wallace (1981), Mulik (1979), or Sawicki (1978).

In spite of these promising reports, early experience in the author's laboratory indicated that further work remained before ion chromatography could be applied routinely to the analysis of oil shale wastewaters. Although the early eluters--$F^-$, $Cl^-$, $NO_2^-$, $PO_4^{3-}$, $SO_3^=$, and $SO_4^=$--could indeed be separated when injected as a pure standard, in real retort wastewaters the $F^-$ and $Cl^-$ peaks were often obscured by additional unknown species. The quantitation of $F^-$ and $Cl^-$ was further complicated by the co-elution of the water dip and carbonate dip (Small et al., 1975). More importantly, after the first injection of real retort waters, subsequent analyses were essentially impossible because of a drifting baseline, presumably due to the elution of highly retained retort water components. Another problem with the direct application of ion chromatography to retort wastewaters was the tailing of $SCN^-$, which significantly decreased its detection limit and increased analysis time.

The effort described in this report was thus directed towards developing and improving ion chromatography for the routine and repetitive analysis of retort wastewaters for non-carbonate anions.

Several different eluents and eluent additives were evaluated for the purpose of improving the $SCN^-$ peak. Solvent programming and non-standard column configurations were also evaluated in an effort to elute $S_2O_3^=$ and $SCN^-$ in reasonable time while still separating the early eluting compounds.

Throughout this effort retort waters were run frequently in order to gain experience with realistic samples.

In order to evaluate various eluents and eluent strengths as efficiently as possible, it is helpful to use the expression (Breyer and Reiman, 1961)

(1) $$t_a = t - t_v = KA^{s/a}$$

where $t_a$ = adjusted retention time

$t_r$ = absolute retention time

$t_v$ = time for one void volume to elute

A = eluent concentration

s, a = valence of sample and eluent, respectively

K = constant for any given resin and eluent

This expression allows retention data to be plotted in a concise manner and permits the estimate of retention times for a variety of conditions based on relatively few measurements. The application of this approach is illustrated in the discussion section of this report.

The following material describes the development of four separate ion chromatographic assays for retort water. The first, termed the "majors protocol", measures the major non-carbonate species normally encountered in retort wastewater--$SO_4^=$, $S_2O_3^=$, and $SCN^-$--as well as $NO_3^-$. The second measures the early eluters but misses $S_2O_3^=$ and $SCN^-$. The third protocol detects $SCN^-$ and $S_2O_3^=$ but misses the early eluters. The final protocol measures total S after digestion with $H_2O_2$.

EXPERIMENTAL

All analyses were performed in a Dionex (Sunnyvale, CA) Model 10 ion chromatograph equipped with an electrical conductivity detector. At the start of this investigation the standard column sequence of injection valve -

precolumn - analytical column - suppressor column - detector was employed. The columns, also supplied by Dionex, were as follows: (1) precolumns, 6 mm × 50 mm, # 30986, fast run type; (2) analytical column, 6 mm × 250 mm, # 30985, fast run type; (3) suppression columns, normal type, 12 mm × 100 mm, #30828. All sample injections were made with a 100 μl sample loop. Peak area and height measurements were accomplished on a Hewlett Packard (Avondale) Model 3390 integrator.

Eluents and standard solutions were made from reagent grade chemicals and deionized, distilled water unless otherwise indicated. Stock standard solutions, from which the working standards were prepared, were prepared at a concentration of 10,000 mg/l, from their Na or K salts. Thiosulfate solutions decomposed in a matter of hours unless prepared in freshly boiled, distilled, deionized water, in which case they were stable for several months. Standards for $SO_3^=$ were prepared from the formaldehyde-bisulfite addition compound $CH_2O:NaHSO_3$ (Aldrich Chemicals). Stock standard solutions prepared from this addition compound were stable for approximately 2 months although working standards in the range 1-100 mg/l had to be prepared fresh daily.

Samples of retort wastewater and steam-stripped retort wastewaters were filtered after collection and stored at 5°C. Before injection into the sample loop, the sample was diluted with d.i., distilled water if necessary and injected through a 0.45 μm pore size membrane filter (Gelman Acrodisc #4184).

The conductivity detector was calibrated periodically with KCl and standards were run before and after each series of analyses and whenever conditions were changed.

During the early stages of this investigation, a rudimentary form of solvent programming was attempted in order to achieve an adequate separation of the early eluters while still eluting $S_2O_3^=$ and $SCN^-$ in reasonable time. Since

the Dionex system is not equipped with solvent programming capabilities, exponential solvent programming was achieved by feeding the high pressure pump from a stirred beaker which in turn was fed from two reservoirs--one containing a strong eluent and the other, the weak eluent. An exponential change in solvent composition was achieved by switching from one reservoir to the other.

Various eluents, including a range of $NaHCO_3$ and $Na_2CO_3$ concentrations, were tested in order to find one capable of separating the early eluters while still eluting $SCN^-$ in a reasonable time. Eluent additives were also evaluated for their ability to improve the $SCN^-$ peak, which tended to tail badly with most eluents. Eluents and additives included $NaHCO_3$ + $Na_2CO_3$ over a range of concentrations; 5 mM $Na_2CO_3$/0.75 mM p-cyanophenol; 20 mM boric acid adjusted to pH 11 with NaOH; 10 mM 4-amino-benzoic acid adjusted to pH 11 with NaOH; 7 mM $Na_2CO_3$ in 10% acetonitrile; 7 mM $Na_2CO_3$/0.75 mM p-cyanophenol; 7 mM $Na_2CO_3$/0.5 mg/l $SCN^-$, added as NaSCN; 10 mM phthalamide adjusted to pH 11 with NaOH; 10 mM n-butylboron adjusted to pH 11 with NaOH; 10 mM succinimide adjusted to pH 11 with NaOH. Methylene-bis-thiocyanate and 2-thiohydantoin were also evaluated as additives to $NaCO_3$.

Because of the long retention times and tailing of thiosulfate and thiocyanate the valve arrangement in the Dionex Model 10 ion chromatograph was modified to that shown in Figure 2-1. Addition of an 8 port slider valve between the load/inject valve and the separator valve enables the sample to progress through both pre-columns and main separator column or only through the pre-columns. The air-driven slider valves are operated under program control of the Hewlett Packard Model 3390 integrator, which operates through a Hewlett Packard Model 19400A Event Control Module and home-made electronic/pneumatic

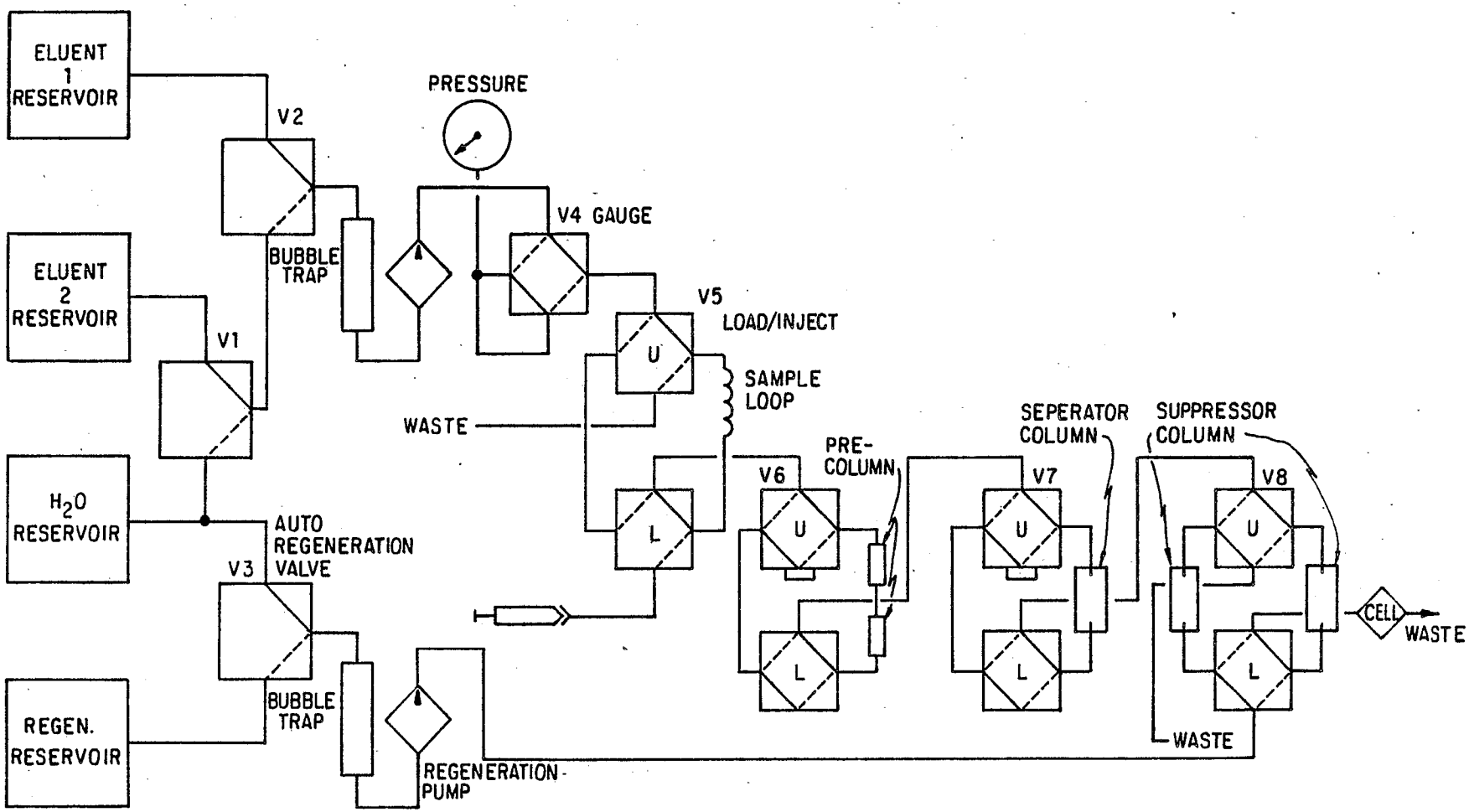


FIGURE 2-1. ION CHROMATOGRAPH VALVE AND COLUMN CONFIGURATION

interface. With this design modification several different protocols were designed and tested, as described below:

1. Major anions. This protocol allows the determination of the major non-carbonate inorganic anions in retort wastewaters--$SO_4^=$, $S_2O_3^=$, and $SCN^-$--during a single run. $NO_3^-$ is also determined.

   For this protocol the sample is injected with both pre-columns and separator columns in line. After four minutes the precolumn is switched out of line (valve V6) leaving $S_2O_3^=$ and $SCN^-$ on the pre-column while the analysis of the earlier species continues on the main analytical column. After the earlier peaks have eluted from the main analytical column (approximately 15 minutes into the run), the main analytical column is switched out of line and the pre-columns are switched in line. $S_2O_3^=$ and $SCN^-$ then elute from the pre-column and proceed directly to the suppressor column. The entire analysis is complete in approximately 35 minutes. The eluent for this procedure is 7.0 mM $CO_3^=$ at a flow rate of 2.3 ml/min.

2. Late eluters. $S_2O_3^=$ and $SCN^-$ are separated and analyzed with the pre-columns switched in-line and the main analytical column switched out of line using an eluent of 7 mM $Na_2CO_3$/0.5 mg/l NaSCN at a flow rate of 2.3 ml/min. $S_2O_3^=$ and $SCN^-$ are well separated while early components elute as a group. The analysis is complete in approximately 15 minutes.

3. Early eluters. The earlier eluting compounds ($Cl^-$ through $SO_4^=$) are separated using 3 mM $Na_2CO_3$ at a flow rate of 2.3 ml/min. This protocol begins with all columns in line. After the early eluters have passed the pre-columns (Ca. 7 minutes), valve V6 is switched to isolate the late eluters, $S_2O_3^=$ and $SCN^-$, on the column while the

analysis of the early eluters proceeds. Immediately before the next sample injection, the pre-columns are switched back in line to retain $S_2O_3^=$ and $SCN^-$ in the next sample.

If the pre-columns were never cleaned, the later eluters would start to bleed onto the main analytical column. This is avoided by rinsing the pre-column with 7 mM $Na_2CO_3$ every third analysis. For this purpose valves V7 and V8 are switched (Figure 2-1), thereby permitting the late eluters to be rinsed to waste, a procedure requiring approximately 10 minutes.

4. Total S. This procedure converts the various forms of S to $SO_4^=$ which is then determined. For this purpose 30% $H_2O_2$ is added to a 25 ml aliquot of sample in an open, stirred, beaker while measuring the Eh with a Pt electrode. $H_2O_2$ is added until the Eh stabilizes at approximately +0.4V vs. an Ag/AgCl electrode. (In practice, 5 ml of $H_2O_2$ is normally more than sufficient.) After allowing the solution to mix for several minutes, it is transferred to a hot plate and boiled for 5 minutes to remove or decompose the $H_2O_2$. After cooling, the solution is transferred to a 100 ml volumetric flask and brought to volume. The resulting solution is analyzed for $SO_4$ using procedure 1 above.

RESULTS AND DISCUSSION

In the Dionex system background conductivity due to the eluent is minimized by passage through the suppressor column, which contains a hydrogen-form cation exchange resin. Nevertheless, a residual conductivity remains due to the partial dissociation of the weakly acidic eluents. In the case of carbonate eluents, the background conductivity is typically 10-20 μ Siemens while peak heights are typically 10-100 μ Siemens.

Original attempts to employ exponential solvent programming with $NaHCO_3/Na_2CO_3$ mixtures resulted in baseline shifts in the electrical conductivity detector which were too large to permit quantitative measurements. Attempts were made to minimize this problem by matching the conductivity of the original and final eluents. In the case of a gradient from $NaHCO_3$ to $Na_2CO_3$ such a matching can in theory be achieved simply by using equal-molar concentrations of each, since the background conductivity is due only to the amount of dissolved $CO_2$ eluting from the suppressor column. When this approach was tried, the initial and final background conductivities were indeed the same; however, an unacceptably large background peak occurred shortly after the $Na_2CO_3$ flow was started, obscuring many of the peaks of interest. This peak can be explained by considering the action of $CO_3^=$ as it encounters the anion exchange resin in the analytical column which has equilibrated with a dilute $HCO_3^-$ eluent. Since $CO_3^=$ is a stronger eluent than $HCO_3^-$, it will displace $HCO_3^-$ from the resin according to the reaction

(2) $$2(R\text{-}HCO_3^-) + CO_3^= \rightarrow R_2CO_3^= + 2HCO_3^-$$

As can be seen, this reaction causes a temporary increase in total carbonate level and hence an increase in background conductivity in the detector. Under the conditions tested, an exponential $NaHCO_3/Na_2CO_3$ solvent gradient was therefore unsatisfactory and was discontinued.

In order to minimize background shifts during gradient programming, a search was made for other possible eluents. Ideally, such an eluent should have a high $pK_a$ in comparison to $H_2CO_3$ ($pK_a = 6.4$) in order to minimize dissociation after the suppressor column. Also, it must be sufficiently soluble in both the acid and ionized form, and be stable in the presence of

air. Of course, a satisfactory eluent must also have a strong enough affinity to the resin to elute the analytes rapidly enough.

Eluents tested for this purpose included hydroquinone ($pK_a$= 10.35), boric acid ($pK_a$= 9.1), 4-aminobenzoic acid, phthalimide, n-butylboron, succinimide, and saccharin (2-sulfobenzoic acid imide). (Acids were converted to the basic form by addition of NaOH.) Each of these proved to be unsatisfactory. Hydroquinone promptly ruined the columns, presumably due to the irreversible attachment of macromolecules which formed due to the exposure of the eluent to air during the preparation process. The background conductivity of saccharin was too high, most likely due to the presence of the sulfonic acid arising from the decomposition of saccharin in basic solution. The other eluents either were too weak or resulted in excessive background conductivity. While the excessive conductivities may have been due to impurities, time did not permit a more exhaustive study of alternate eluents.

Because of the apparent difficulty of finding an eluent system suitable for solvent programming, efforts were directed towards optimizing the $NaHCO_3/Na_2CO_3$ eluent for retort waters. The first problem was the tailing of the $SCN^-$ peak with the standard eluent (2.4 mM $NaHCO_3$/3 mM $Na_2CO_3$). To minimize tailing two approaches were tried: (1) the use of stronger eluents, and (2) the addition of trace species which resemble the $SCN^-$. The latter approach is based on the supposition that the $SCN^-$ tailing is due to the presence of a minority of sites which bind $SCN^-$ more tightly and which may be blocked through the action of similar species. Additives to $Na_2CO_3$ included p-cyanophenol, 2-thiohydantoin, acetonitrile, methylene-bis-thiocyanate, and NaSCN. Of these, the first three additives showed no effect. The fourth additive caused a slight improvement, but the most significant improvement was for 0.5 mg/l $SCN^-$ in 7 mM $Na_2CO_3$. Figure 2-2 compares the elution of $SCN^-$

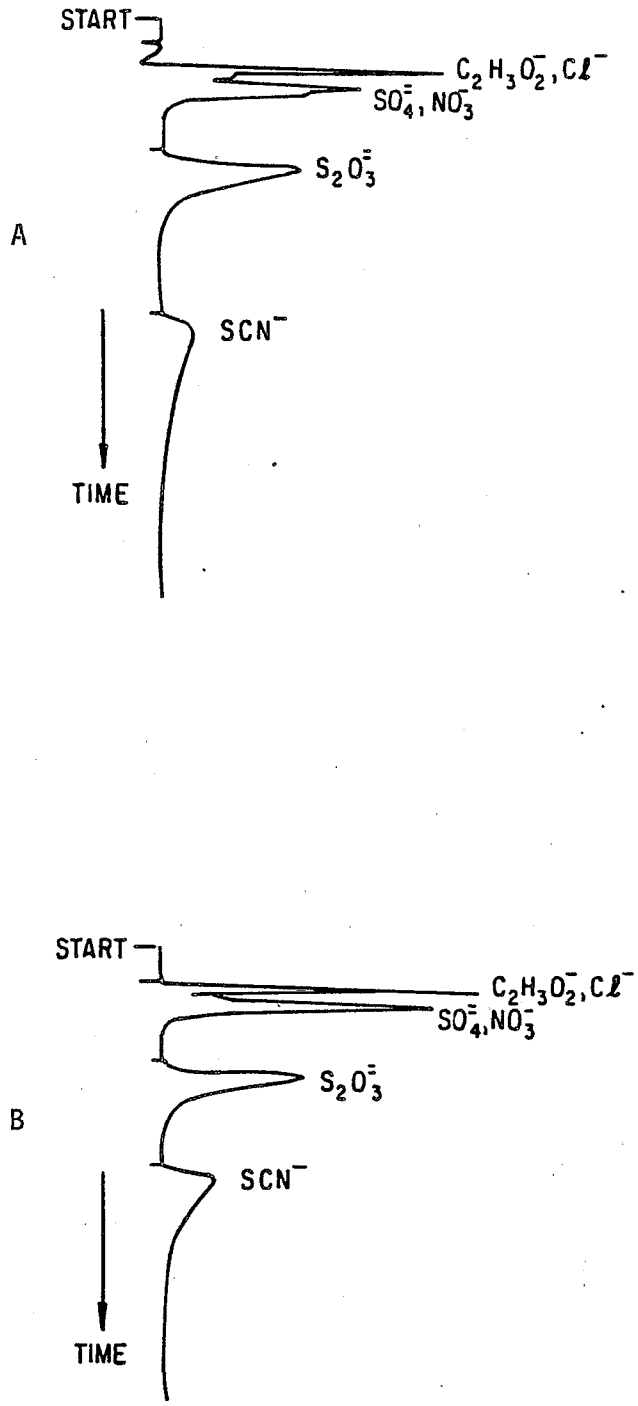


FIGURE 2-2

Ion chromatograph of $S_2O_3^=$ and $SCN^-$ in retort waters

A. Eluent = 7mM $Na_2CO_3$

B. Eluent = 7mM $Na_2CO_3$ + 0.5 mg/l Na SCN

using this eluent with two pre-columns. As can be seen, NaSCN both increases the eluent strength and improves the $SCN^-$ peak. For this reason the 7 mM $NaCO_3$/0.5 mg/l NaSCN eluent was chosen as optimum for $SCN^-$.

In order to more systematically develop a separation with the $NaHCO_3/Na_2CO_3$ eluent system, the retention times for the ions of interest were measured and plotted against eluent concentration, as shown in Figure 2-3. As is illustrated for the case of $Cl^-$, $NO_2^-$, $NO_3^-$, and $SO_4^=$, the retention times vary with eluent strength as predicted by equation 1. Thus, if the retention times for the ions of interest are known at one eluent strength and column length, retention times can be predicted over a range of concentration and column lengths. Next, this relationship was used to most efficiently select an eluent to separate the desired species.

The utility of equation 1 is further illustrated by Figure 2-4, which includes retention data for three different eluents: $NaHCO_3$, equimolar $NaHCO_3/Na_2CO_3$, and $Na_2CO_3$. In this figure the abscissa for each of the eluents is shifted in order to make the retention times overlap. One of the first observations in Figure 2-4 is that the strength of the equimolar $NaHCO_3/Na_2CO_3$ eluent is almost exactly one-half that of the $Na_2CO_3$ eluent. This implies that the $NaHCO_3$ component in the former solution is not active in displacing the analyte ions from the resin. However, the $NaHCO_3$ component nevertheless contributes to background conductivity and shortens the suppressor lifetime. For these reasons $NaHCO_3$ was dropped from future eluents for most samples.

Figure 2-4 also suggests that much of the strength of the $NaHCO_3$ eluent is due to the presence of carbonates. Were $HCO_3^-$ the only eluent ion binding to the resin, the slopes for the monovalent ions would be -1. Instead, their measured slopes are approximately -0.7, suggesting a mixed eluent system.

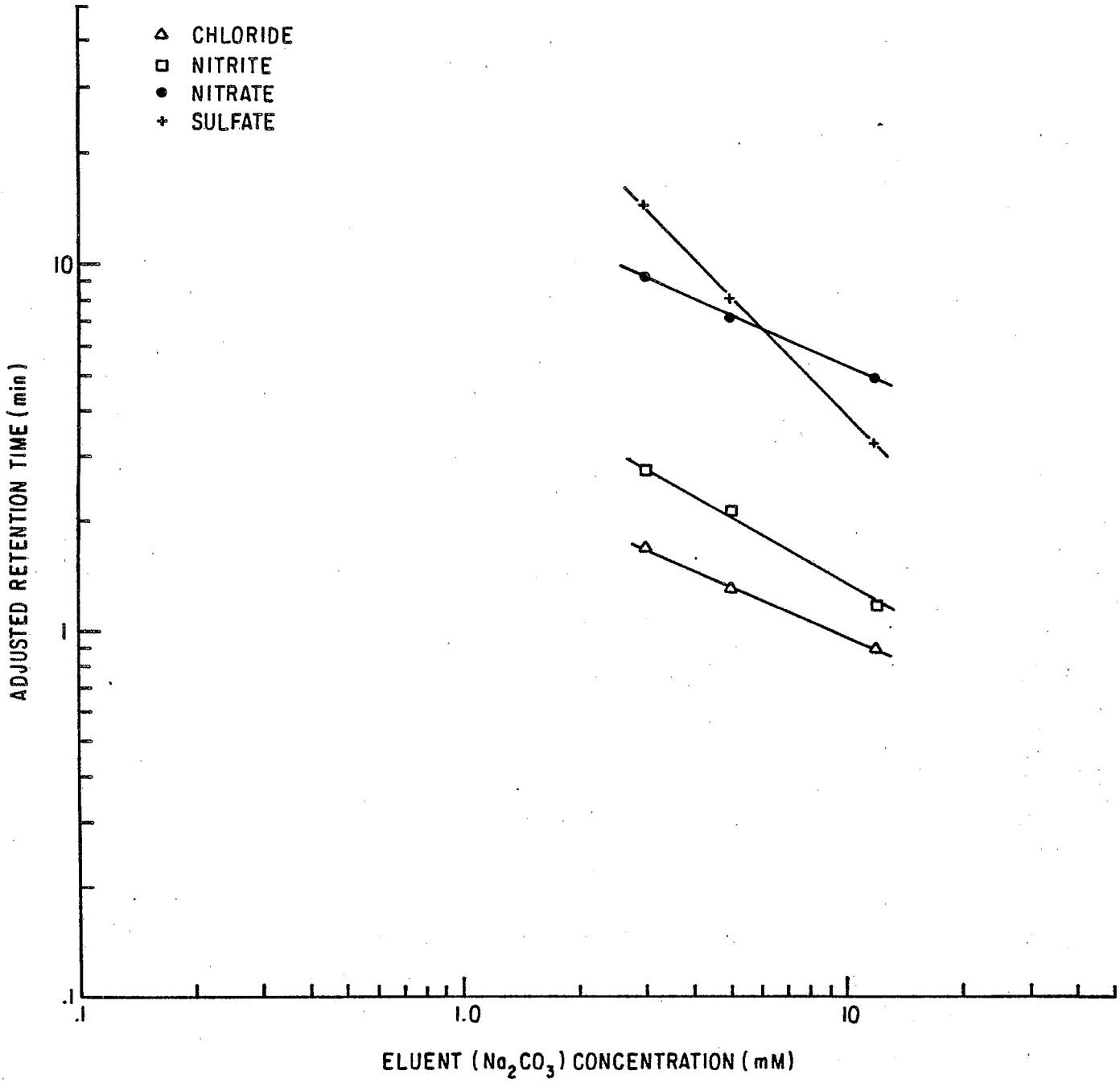


FIGURE 2-3

Variation of adjusted retention time with eluent strength

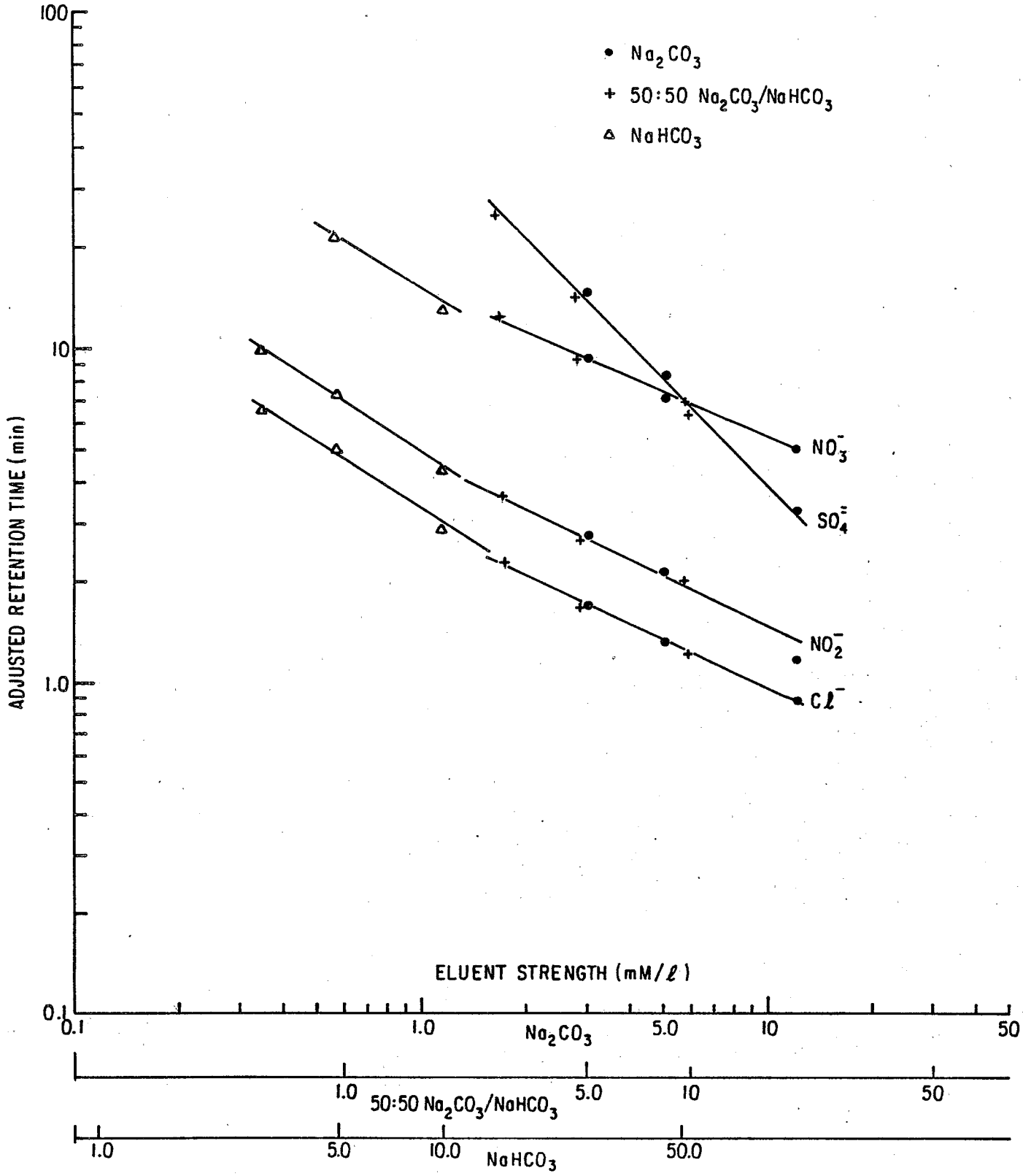


FIGURE 2-4. ADJUSTED RETENTION TIMES FOR THREE ELUENTS

A more thorough examination of the derivation of equation 1 (Reiman, 1961) would indicate that the constant K can be factored into two parts, $K_s$ and $K_a$, where $K_s$ depends only on the sample ion and $K_a$, only on the eluent ion. Equation 1 can then be written as

$$\log t_r = \log K_s + \log K_a - \left(\frac{s}{a}\right) \log A \tag{3}$$

While the absolute values of $K_s$ and $K_a$ cannot be known, relative values of $K_s$ for a given column material can be assigned by injecting a series of ions while keeping the eluent constant. Once relative values of $K_s$ are assigned for one eluent, other eluents can be evaluated, at least in theory, by measuring the retention time of a single sample ion, at which point the retention times can be calculated for the other ions.

In practice the approach described mathematically in the previous paragraph can be most readily implemented graphically, as is illustrated in Figure 2-4. Once retention times are measured at a few points, they can be plotted linearly on log-log graph paper in order to establish the expected retention times over a range of conditions. A new eluent can readily be evaluated by injecting a few ions, at which point the corresponding retention times for other ions can be graphically calculated by plotting the data as shown in the figure. Retention times for other column lengths can also be estimated since $t_r$ is proportional to column length, all else being equal.

While equation 3 and the associated graphical approach provide a systematic basis for optimizing a separation, the practitioner must be aware of additional factors. First, besides the eluent strength, other variables may be manipulated in order to achieve the desired separation, including pH, temperature, the presence of chelating agents, and column materials. Second,

in the authors' experience, equation 3 is not necessarily obeyed exactly, and therefore the chromatographic conditions must be tested close to the conditions finally selected. Third, the previous paragraphs take no account of peak shape or tailing, which must often be considered on an individual basis.

Using the approach described in the previous paragraph, four protocols were developed for the ions encountered in retort wastewater. Since the late eluters $S_2O_3^=$ and $SCN^-$ could not be separated in a reasonable time under the same conditions as the early eluters, the column switching procedure described in the experimental section of this report was developed for the major species.

Figure 2-5 shows a chromatogram of a typical retort water sample analyzed with the majors protocol. Although a peak is often observed near 4.9 minutes, $Cl^-$ and acetate are not adequately resolved in this region of the chromatogram so that definitive assignment is not possible. (Occasionally retort waters are encountered which give a much broader peak at 4.9 minutes, suggesting the presence of mixed organic acids.) With the retort waters encountered in the authors' laboratory, the region between the $Cl^-/Ac^-$ peak and the $SO_4^=$ peak is normally empty, indicating the absence of $SO_3^-$, $NO_2^-$, and $PO_4^{3-}$. However, when a peak occasionally does occur in this region, definitive assignment requires the use of a weaker eluent. If enough information is known about the sample to exclude two of the possible three ions in this region, analysis could proceed for peaks occurring between $Cl^-$/acetate peak and the $SO_4^=$ peak. As indicated in the figure, $SO_4^=$, $S_2O_3^=$, and $SCN^-$ are clearly resolved during a time period of approximately 30 minutes. $NO_3^-$, although normally not observed in retort wastewaters in significant amounts, occurs immediately after $SO_4^=$. The separation of $NO_3^-$ from $SO_4^=$ is adequate for quantitation when $NO_3^-$ is present in significant amounts.

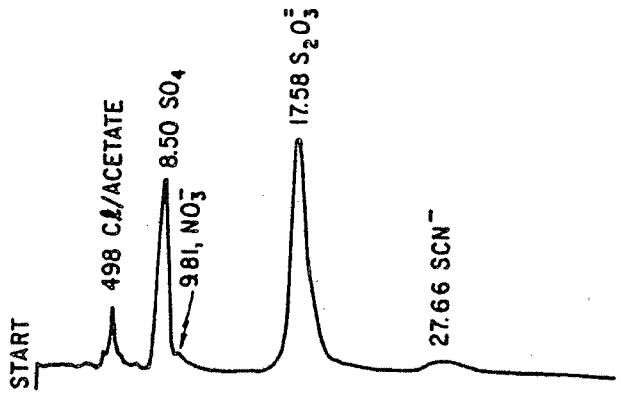


FIGURE 2-5

Ion chromatogram of a retort wastewater using the majors protocol

Figure 2-6 shows calibration curves for $Cl^-$, $NO_3^-$, $SO_4^=$, $S_2O_3^=$, and $SCN^-$ obtained with the majors protocol. For these species the calibration curves are linear over the range 3-100 mg/l. At higher concentrations the retention times tend to decrease, especially for the late eluters, making peak identification less certain. At lower levels baseline drift limits detectability. Either peak height or peak area can be used for quantitation, although peak height is normally less subject to interference due to nearby peaks.

When $S_2O_3^=$ and $SCN^-$ are the only species of interest, the most rapid method is to use 7 mM $NaCO_3$ with 0.5 mM NaSCN as the eluent, which minimizes tailing of the $SCN^-$ peak, with only the two pre-columns in line. Under these conditions acetate through nitrate elute unresolved in about 4 minutes, while $S_2O_3^=$ and $SCN^-$ elute in approximately 8 and 15 minutes respectively (Figure 2-2b). Figure 2-7 shows calibration curves over the concentration range 1-300 mg/l. While linear over most of the range, slight curvature is apparent between 100 and 300 mg/l. This curvature is most likely explained by initial column saturation effects, especially since elution times start to decrease at 300 mg/l.

The third protocol is for the early eluters, acetate - $SO_4^=$, including $NO_3^-$, which elutes before $SO_4^=$ with the eluent used for this protocol. As described in the Experimental section of this report, and as normally practiced in the authors' laboratory, this procedure employs 3 mM $Na_2CO_3$. However, as will be seen in the following discussion, this eluent concentration is not appropriate in every situation and must be adapted to sample requirements, although the valving sequence can remain basically unchanged. It is therefore proposed that the analyst use this basic procedure for measuring the early eluters in retort water, but that he be prepared to alter the eluent to meet

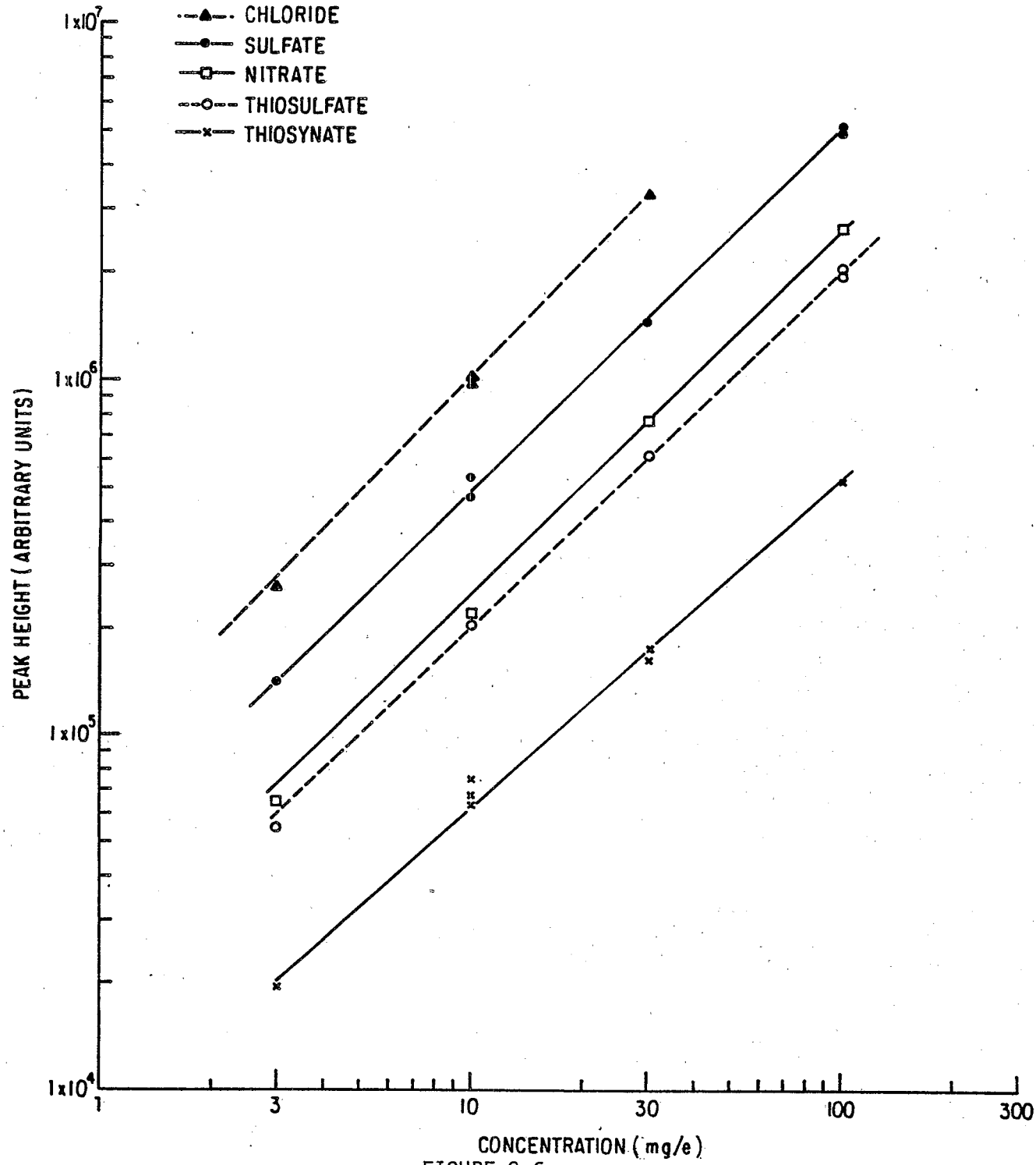


FIGURE 2-6

Calibration curves obtained with the majors protocol for $Cl^-$, $NO_3^-$, $SO_4^=$, $S_2O_3^=$, and $SCN^-$

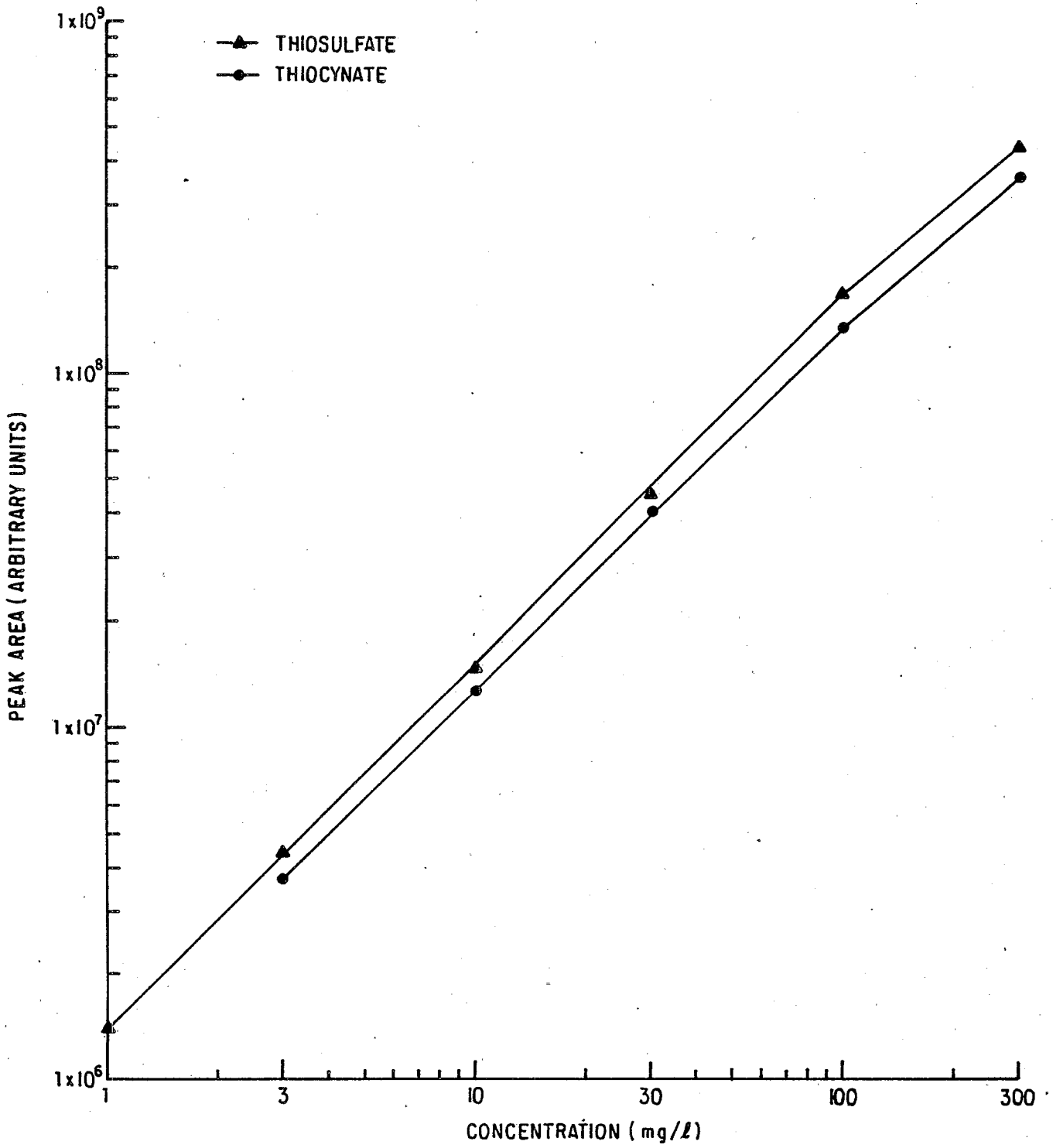


FIGURE 2-7

Calibration curves obtained with the protocol for late eluting compounds

sample requirements. The following discussion summarizes information of which the analyst should be aware to obtain acceptable results.

Figure 2-8 contains chromatograms obtained with this protocol using two different eluents. The first chromatogram shows an adequate separation of acetate, $Cl^-$, $NO_2^-$, $SO_3^=$, and $SO_4^=$ using 3 mM $Na_2CO_3$. Comparison of the first and second chromatograms illustrates one of the first problems with the early eluters: the position of the acetate peak depends not only on the eluent strength, but also on the condition of the suppressor column, moving to an earlier position as the suppressor column is exhausted. This phenomenon is due to the retention of acetate by the hydrogen-form but not the sodium-form of resin in the suppressor column by ion exclusion effects. The analyst hoping to determine both acetate and $Cl^-$ clearly must consider this possible interference. Another potential difficulty with $Cl^-$ and acetate is that their position is near the water and carbonate dips, which appear as negative peaks near the start of the chromatogram. Depending on the concentration range of acetate and $Cl^-$, these peaks must be separated through proper selection of eluent and column in order to obtain quantitative results (Stevens et al., 1981). In practice, interferences due to carbonate and acetate can be minimized by minimizing ion exclusion effects in the suppressor columns, for example, by using a sufficiently short suppressor column. (Unfortunately, shorter suppressor columns require more frequent regeneration.) Another approach to eliminating the migration of the carbonate and acetate peaks is the use of a fiber suppressor column, for which retention by ion exclusion does not occur (Stevens et al., 1981). Thus, while the analysis for $Cl^-$ and acetate should be approached with caution, careful column selection should make these determinations feasible.

FIGURE 2-8
(Cont'd on next page)

Ion chromatograms of standards obtained using the early eluter protocol

A. eluent = 3 mM $Na_2CO_3$, suppressor column almost spent

B. same conditions as A, regenerated suppressed column

C. standard eluent (2.4 mM $Na_2CO_3$/3.0 mM $NaHCO_3$)

D. same as C, but sample also contains $SO_3^=$

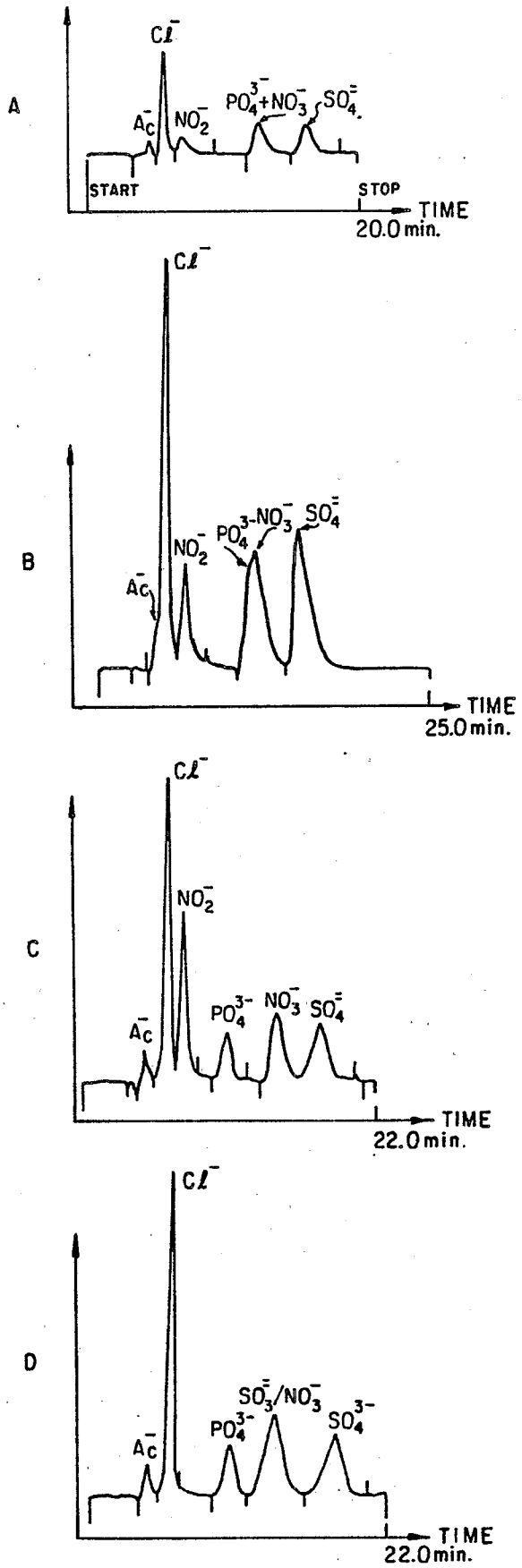
A
Cl⁻
Ac⁻
NO₂⁻
PO₄³⁻+NO₃⁻
SO₄⁻⁻
START
STOP
TIME
20.0 min.
B
Cl⁻
Ac⁻
NO₂⁻
PO₄³⁻-NO₃⁻
SO₄⁻⁻
TIME
25.0 min.
C
Cl⁻
NO₂⁻
Ac⁻
PO₄³⁻
NO₃⁻
SO₄⁻⁻
TIME
22.0 min.
D
Cl⁻
Ac⁻
PO₄³⁻
SO₃⁻⁻/NO₃⁻
SO₄³⁻
TIME
22.0 min.

Figure 2-8d illustrates another potential interference. With a 3 mM $Na_2CO_3$ eluent, $SO_3^=$ co-elutes with $NO_3^-$ and $PO_4^{3-}$. However, for the retort waters encountered in the authors' laboratory, this potential interference has not posed a problem since the retort wastewaters encountered have contained neither $PO_4^{3-}$ nor $NO_3^-$ in significant amounts. Furthermore, this protocol is normally carried out only after the "majors analysis" has been completed, so that the absence of $NO_3^-$ has already been established. However, should $PO_4^{3-}$ be present, perhaps as an additive to a biological reactor, its peak can be displaced by adjusting the pH, as is illustrated in Figure 2-8c. In this figure acetate, $Cl^-$, $NO_2^-$, $PO_4^{3-}$, $SO_3^=$, and $SO_4^=$ are separated using an eluent of 2.4 mM $Na_2CO_3$/3.0 mM $NaHCO_3$, although $NO_3^-$ would still not be adequately separated from $SO_3^=$.

Figure 2-9 illustrates the adjusted retention times for seven early eluters obtained with eluents of various strengths containing $Na_2CO_3$ and $NaHCO_3$ in a ratio of 2.4/3.0 on a fast run column. In using this diagram it should be kept in mind that the position of the $PO_4^{3-}$ peak can also be adjusted relative to the other peaks by varying the pH of the eluent. This diagram suggests that the best separation of the seven early eluters could be obtained with an eluent of 1.4 mM $Na_2CO_3$/1.8 mM $NaHCO_3$. (Such a separation is shown in Figure 2-8d and indicates that the separation of $NO_3^-$ and $So_4^=$ is not yet complete.) Figure 2-10 demonstrates calibration curves for the early eluters (with the exception of $NO_3^-$) obtained with this protocol.

The measurement of total sulfur, the fourth procedure reported, serves as a check on the completeness of the analyses of the individual S species. This procedure, as described in the Experimental section of this report, involves no new chromatographic procedure, but only an oxidation with $H_2O_2$.

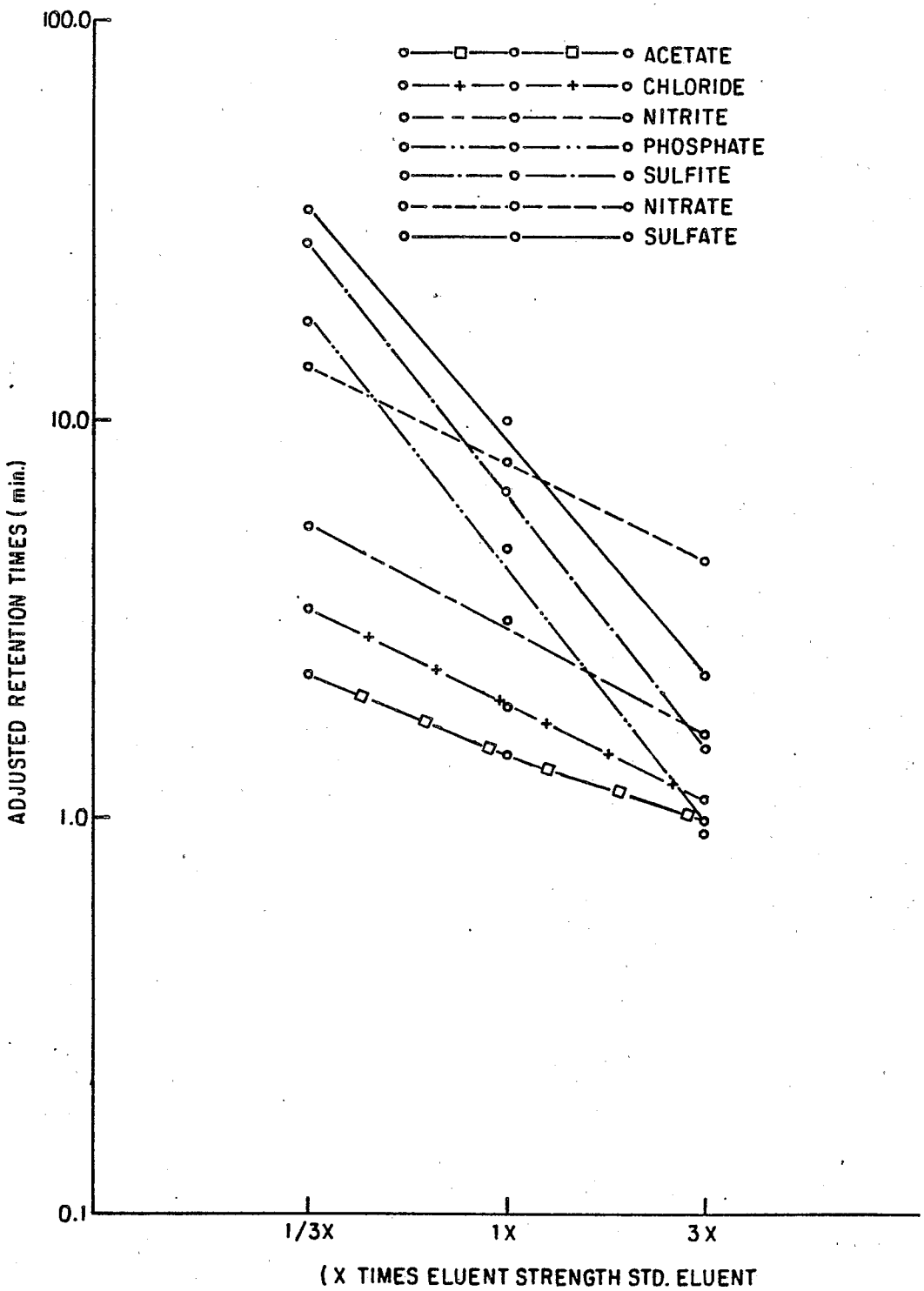


FIGURE 2-9

Adjusted retention times for seven ions with standard eluent (2.4 mM $CO_3^{=}$ + 3.0 mM $HCO_3^{-}$)

The effect of this oxidation is shown in Table 2-1 for four retort water samples. The original concentrations of $S_2O_3^=$, $SO_4^=$, and $SO_3^=$ were measured using the "majors protocol"; $S^=$ and $SO_3^=$, which were absent in the original samples, were added using standard solutions. Closure is within experimental error, which supports the validity of the individual determinations obtained with the "majors protocol", as well as the oxidation procedure. Because of the possibility of occurrence of other, unexpected S species in retort wastewaters, it is recommended that the total S measurement be run periodically.

In the authors' laboratory, retort waters are analyzed routinely by ion chromatography for $SO_4^=$, $NO_3^-$, $S_2O_3^=$, and $SCN^-$ and occasionally for $Cl^-$, using the procedures described above. Other than the occasional replacement of a precolumn, no unusual problems have arisen. The precision for $S_2O_3^=$, $SCN^-$, and $SO_4^=$ averages 3% relative (1 $\sigma$) at naturally occurring concentrations. The precision (1 $\sigma$) of the $NO_3^-$ measurement is poorer (9% relative) at naturally occurring levels, as would be expected for the low levels normally encountered (Figure 2-5). The precision of the $Cl^-$ measurement averages 8% (1 $\sigma$), which is somewhat less than ideal due to the variable occurrence of the interfering carbonate dip. Recovery of $SO_4^=$, $NO_3^-$, $S_2O_3^=$, $SCN^-$, and $Cl^-$ spiked into retort waters is normally 100% within experimental error. As of this writing, insufficient data have been gathered to establish statistical parameters for other species.

PROTOCOL FOR MAJOR ANIONS ANALYSIS

Principle

The major anions in retort wastewaters are separated and quantitated by ion chromatography, a form of high pressure liquid chromatography. In this method the various anions are separated on a surface-agglomerated anion exchange resin with an eluent of sodium carbonate. The eluent from the first

Table 2-1

OXIDATION BY $H_2O_2$ OF VARIOUS S SPECIES TO $SO_4^=$

| Sample No. | S-8 | S-5 | S-6 | 10/6 Feed |
|---|---|---|---|---|
| Original Species | | | | |
| $SO_4^=$ (mg/l) | 15.5 | 18.0 | 18.0 | 33.5 |
| $S_2O_3^=$ (mg/l) | 45.0 | 50.0 | 32.5 | 24.0 |
| $SCN^-$ (mg/l) | 7.3 | 7.5 | 6.3 | 5 |
| $SO_3^=$ (mg/l) | 50.0 | 100.0 | 50.0 | 30 |
| $S^=$ (mg/l) | 50.0 | 100.0 | 50.0 | |
| Theoretical yield of $SO_4^=$ (mg/l) | 314 | 537 | 294 | 119 |
| Measured yield of $SO_4^=$ (mg/l) | 340 | 525 | 315 | 125 |
| Measured yield of $SO_4^=$ (%) | 108 | 98 | 107 | 105 |

(separator) column proceeds to a second ion exchange column in the $H^+$ form where the eluent is converted to the weakly ionized hydrogen form. From the second column the eluent proceeds to a low dead-volume electrical conductivity cell where the analytes are detected as their strong acids.

For this protocol the major anions elute in the order sulfate, nitrate, thiosulfate, and thiocyanate. (Carbonate/bicarbonate are not detected.) Sulfite is also detected prior to the sulfate peak but has not yet been shown to be entirely interference free. The earlier components (e.g. acetate, chloride, phosphate, nitrite) elute as an unresolved group. Column switching is necessary to achieve the separation described in this protocol.

Equipment

Dionex Ion Chromatograph with auxillary valve installed as shown in Figure 2-1

Integrator - such as HP 3390

2 - Dionex Fast Run Pre-Columns 3×150 mm

1 - Dionex Fast Run Anion Column 3×500 mm

1 - Dionex Anion Suppressor Column 6×25 mm

3 - 4 liter carboys

1 - 1 liter volumetric flasks

10 - 100 milliliter volumetric flasks

1 - 500, 100 and 10 milliliter graduated cylinder

10 cubic centimeter disposable syringes

0.45 μm syringe filters

1 - variable pipettor 100-1,000 μl

pipettors - 10 μl and 30 μl

3 cycle logarithmic paper

Reagents

1. 0.01 N KCl - Potassium Chloride Stock Standard

   Dry KCl in oven at 105° to constant weight at 20°C. Weigh out 0.7456 grams of KCL and add to 500 ml of distilled water in a 1 liter volumetric flask. Shake to dissolve KCl and bring up to volume with distilled water.

2. 0.001 N KCl - Potassium Chloride Calibration Standard

   Measure 400 ml of 0.01 N KCl stock standard and add to 3,500 ml distilled water in 4 liter carboy. Mix solution and dilute to volume with distilled water.

3. 0.007 M $Na_2CO_3$

   Measure 2.3744 grams of ACS grade $Na_2CO_3$ on an analytical balance. Add to distilled water in 4 liter carboy and dilute to volume with distilled water.

4. 1 M $H_2SO_4$ - Regeneration Solution

   Measure 111 ml of concentrated sulfuric acid with graduated cylinders. Dilute to 4 liters in carboy using distilled water.

5. Anion Stock Standards - 10,000 mg/l

   a. Chloride - measure 1.6484 grams NaCl on an analytical balance. Dissolve in 100 ml volumetric flask using distilled water. Dilute to volume.

   b. Sulfite - measure 1.7089 grams 98% formaldehyde sodium bisulfite addition complex and dissolve in 100 ml volumetric flask with distilled water. Bring up to volume with distilled water.

   c. Sulfate - measure 1.8142 grams $K_2SO_4$ on an analytical balance. Dissolve in 100 ml volumetric and bring up to volume with distilled water.

d. Nitrate - measure 1.3708 grams $NaNO_3$ on an analytical balance. Dissolve in a 100 ml volumetric flask and bring up to volume with distilled water.

e. Thiosulfate - measure 1.4101 grams $Na_2S_2O_3$ on an analytical balance. Dissolve in a 100 ml volumetric flask and bring up to volume with distilled water.

f. Thiocyanate - measure 1.3958 grams sodium thiocyanate on an analytical balance. Dissolve in a 100 ml volumetric flask and bring up to volume with distilled water.

6. Working Standards

1 ppm - using pipettor add 10 µl of each anion stock standard to a 100 ml volumetric and dilute to volume with distilled water.

3 ppm - as above using 30 µl pipettor

10 ppm - 100 µl each

30 ppm - 300 µl each

100 ppm - 1,000 µl each

Procedure

1. Pretreatment of Sample. Dilute sample if a concentration of greater than 100 mg/l of any component of interest is expected.

2. Preliminary Procedures

a. Calibrate conductivity meter using 0.001 N KCl solution with pre-columns, anion column and anion suppressor column out of line. Reading should be 147 ± 2 µmhos/cm. If not within acceptable range, follow conductivity meter instructions for correcting the reading.

b. Prepare calibration plot using the following protocol. The system should be set up so that the pre-columns, the main

separator column and the suppressor column are separately controlled (Figure 2-1). Before injection of a standard, all three columns should be in the sample stream. Four minutes after injection the pre-column should be taken out of line to trap the thiosulfate and thiocyanate on the pre-column. Chloride, sulfide, sulfate and nitrate will elute in 11 minutes. At that time the main separator should be switched out of line and the pre-columns back in line. The thiosulfate and thiocyanate will now elute. The complete analysis takes approximately 35 minutes. The anion standards should be run twice for each concentration and the resulting peak height plotted against the concentration on log-log paper. The calibration graph should be linear with a slope close to one.

3. Sample analysis. Inject diluted sample onto sample loop through a 0.45 μl syringe filter to remove particulate matter. Follow the same procedure as for the anion standards. The concentrations are determined by comparing the peak heights to the calibration curve.

Interferences

Acetate and other weakly acidic organic acids can coelute under some conditions with chloride. Also, a carbonate dip can occur if the carbonate concentration in the sample is much smaller than in the eluent. This dip occurs just before the chloride peak and can interfere with chloride peak height measurement. It can be minimized by adjusting the sample carbonate concentration to equal the eluent. Acetate will sometimes co-elute with chloride depending on the state of the suppressor column. (See text).

Species eluting prior to $SO_4^=$ are not entirely resolved, so that in the presence of more than one of these anions the sample must be run using a weaker eluent such as 1.8 mM $NaHCO_3$ and 1.4 mM $Na_2CO_3$.

PROTOCOL FOR THIOSULFATE AND THIOCYANATE

Principle

Thiosulfate and thiocyanate are separated and quantitated by ion chromatography, a form of high pressure liquid chromatography. In this method the various anions are separated on a surface agglomerated anion exchange resin with an eluent of sodium carbonate/Na SCN. The eluent from the separator column proceeds to a second ion exchange column in the $H^+$ form where the eluent is converted to the weakly ionized carbonic acid and the sample ions are converted to the hydrogen form. From the second column the eluent proceeds to a low dead-volume electrical conductivity cell where the analytes are detected as their ions.

Equipment

Dionex Ion Chromatograph

Integrator - such as HP 3390

2 - Dionex Fast Run Pre-Columns 3×150 mm

1 - Dionex Anion Suppressor Column 6×25 mm

3 - 4 liter carboys

1 - 1 liter volumetric flask

4 - 100 milliliter volumetric flasks

1 - 500, 100, and 10 milliliter graduated cylinder

10 cubic centimeter disposable syringes

0.45 μm syringe filters

1 - variable pipettor 100-1,000 µl

1 - pipettor - 10 µl and 30 µl

3 cycle logarithmic paper

Reagents

1. 0.01 N KCl - Potassium Chloride Stock Standard

   Dry KCl in oven at 105° to constant weight at 20°C. Weigh out 0.7456 grams of KCl and add to 500 ml of distilled water in a 1 liter volumetric flask. Shake to dissolve KCl and bring up to volume with distilled water.

2. 0.001 N KCl - Potassium Chloride Calibration Standard

   Measure 400 ml of 0.01 N KCl stock standard and add to 3,500 ml distilled water in 4 liter carboy. Mix solution and dilute to volume with distilled water.

3. 0.007 M $Na_2CO_3$

   Measure 2.3744 grams of ACS grade $Na_2CO_3$ on an analytical balance. Add to distilled water in 4 liter carboy and dilute to volume with distilled water.

4. 1 M $H_2SO_4$ - Regeneration Solution

   Measure 111 ml of concentrated sulfuric acid with graduated cylinders. Dilute to 4 liters in carboy using distilled water.

5. Anion Stock Standards - 10,000 ppm

   a. Thiosulfate - measure 1.4101 grams $Na_2S_2O_3$ on an analytical balance. Dissolve in 100 ml volumetric and bring up to volume with distilled water.

   b. Thiocyanate - measure 1.3958 grams NaSCN on an analytical balance. Dissolve in 100 ml volumetric and bring up to volume with distilled water.

6. Working Standards

   1 ppm - using pipettor add 10 µl of each anion stock standard to a 100 ml volumetric and dilute to volume with distilled water.

   3 ppm - as above using 30 µl pipettor

   10 ppm - 100 µl each

   30 ppm - 300 µl each

   100 ppm - 1,000 µl each

Procedure

1. Pretreatment of Sample: dilute sample if a concentration greater than 100 mg/l of any component of interest is expected.
2. Preliminary Procedures
   a. Calibrate conductivity meter using 0.001 N KCl solution with pre-columns, anion column and anion suppressor column out of line. Reading should be 147 ± 2 µmhos/cm. If not within acceptable range, follow conductivity meter instructions for correcting the reading.
   b. Prepare calibration graph by running the anion standard series twice and plotting the resultant peak heights versus the anion concentrations on logarithmic paper. Note that only the two pre-columns are used as separator columns. Each analysis should take approximately 20 minutes.
3. Sample Analysis: inject diluted sample onto sample loop through a 0.45 µm syringe filter to remove particulate matter. Follow the same procedure as for the anion standards. The actual concentrations are determined by comparing the peak heights to the calibration curve.

PROTOCOL FOR EARLY ELUTING SPECIES

Principle

The major anions in retort wastewaters are separated and quantitated by ion chromatography, a form of high pressure liquid chromatography. In this method the various anions are separated on a surface-agglomerated anion exchange resin with an eluent of sodium carbonate. The eluent from the first (separator) column proceeds to a second ion exchange column in the $H^+$ form where the eluent is converted to the weakly ionized hyrogen form. From the second column the eluent proceeds to a low dead volume electrical conductivity cell where the analytes are detected as their strong acids.

For this protocol the late eluters, which would otherwise bleed from the column during subsequent analyses, are trapped on a precolumn while the early eluters proceed to analysis. The precolumn is periodically flushed to waste without upsetting the baseline from the analytical column. This procedure requires that a timed valve switching sequence be performed during the separation. While this valve sequence can remain unchanged, the analyst should be prepared to adjust the eluent strength slightly (based on sample characteristics) in order to achieve the optimum separation.

Equipment

Dionex Ion Chromatograph with valves and columns arranged as shown in Figure 2-1

Integrator - such as HP 3390

2 - Dionex Fast Run Pre-Columns 3×150 mm

1 - Dionex Fast Run Anion Column 3×500 mm

1 - Dionex Anion Suppressor Column 6×25 mm

3 - 4 liter carboys

1 - 1 liter volumetric flask

6 - 100 milliliter volumetric flasks

1 - 500, 100 and 10 milliliter graduated cylinder

10 cubic centimeter disposal syringes

0.45 μm syringe filters

1 - variable pipettor 100-1,000 μl

1 - pipettor - 10 μl and 30 μl

3 cycle logarithmic paper

Reagents

1. 0.01 N KCl - Potassium Chloride Stock Standard

   Dry KCl in oven at 105° to constant weight at 20°C. Weigh 0.7456 grams of KCl and add to 500 ml of distilled water in a 1 liter volumetric flask. Shake to dissolve KCl and bring to volume with distilled water.

2. 0.001 N KCl - Potassium Chloride Calibration Standard

   Measure 400 ml of 0.01 N KCl stock standard and add to 3,500 ml distilled water in 4 liter carboy. Mix solution and dilute to volume with distilled water.

3. 0.003 M $Na_2CO_3$ - Weak Eluent

   Measure 1.0176 grams of ACS grade $Na_2CO_3$ on an analytical balance. Add to distilled water in 4 liter carboy and dilute to volume with distilled water.

4. 1 M $H_2SO_4$ - Regeneration Solution

   Measure 111 ml of concentrated sulfuric acid with graduated cylinders. Dilute to 4 liters in carboy using distilled water.

5. Anion Stock Standards - 10,000 mg/l

   a. Chloride - measure 1.6484 grams NaCl on an analytical balance. Dissolve in 100 ml volumetric using distilled water. Dilute to volume.

   b. Sulfite - measure 1.7089 grams 98% formaldehyde sodium bisulfite addition complex and dissolve in 100 ml volumetric flask with distilled water. Bring to volume with distilled water.

   c. Sulfate - measure 1.8142 grams $K_2SO_4$ on an analytical balance. Dissolve in 100 ml volumetric and bring to volume with distilled water.

6. Working Standards

   1 mg/l - using pipettor add 10 µl of each anion stock standard to a 100 ml volumetric and dilute to volume with distilled water.

   3 mg/l - as above using 30 µl pipettor

   10 mg/l - 100 µl each

   30 mg/l - 300 µl each

   100 mg/l - 1,000 µl each

Procedure

1. Pretreatment of Sample: Dilute sample if a concentration greater than 100 mg/l of any component of interest is expected.

2. Preliminary Procedures

   a. Calibrate conductivity meter using 0.001 N KCl solution with pre-columns, anion column and anion suppressor column out of line. Reading should be 147 ± 2 µmhos/cm. If not within acceptable range, follow conductivity meter instructions for correcting the reading.

b. Prepare a calibration curve using the working anion standards. With the columns in line, pump eluent through system until baseline stabilizes. Zero the meter. Flush sample loop and inject 1 ppm standard. The standard run should take approximately 15 minutes. Complete the anion standard series, running each twice. Plot the resulting peak height vs. concentration on log-log paper. The calibration curve should be linear and close to a slope of one.

3. Sample Analysis

Inject diluted sample onto sample loop through a 0.45 μm syringe filter to remove particulate matter. Determine concentrations by comparing the peak heights to the calibration curve.

Interferences

Acetate and other weakly acidic organic acids can coelute under some conditions with chloride. Also, a carbonate dip can occur if the carbonate concentration in the sample is much smaller than in the eluent. This dip occurs just before the chloride peak and can interfere with chloride peak height measurement. It can be minimized by adjusting the sample carbonate concentration to equal the eluent.

Phosphate, sulfite and nitrate coelute with 3 mM $Na_2Co_3$ eluent, so in the presence of more than one of these anions the use of another eluent such as 1.8 mM $NaHCO_3$, 2.4 mM $Na_2CO_3$ is recommended.

PROTOCOL FOR TOTAL SULFUR

Principle

Total sulfur in water is measured by oxidation of the sulfur species to sulfate and quantitation of the sulfate by ion chromatography.

Equipment

Electrometer - reading to 0.1 volts

Platinum wire electrode

Reference electrode

Magnetic stirrer

stir bars

buret - 10 ml

25 ml pipets

100 ml beakers

hot plate, watch glass

100 ml volumetric

Reagents

30% $H_2O_2$ (fresh)

Sample Pre-treatment

Put 25 ml of sample into a 100 ml beaker. Place platinum wire electrode and reference electrode in the sample. Connect electrodes to electrometer. Stir the sample with a magnetic stirrer. Note the initial electrical potential, then begin adding 30% $H_2O_2$ dropwise from the buret. Continue adding the 30% $H_2O_2$ until the oxidation potential is +0.4V. At this potential all sulfur species will have oxidized to $SO_4$.

Heat the oxidized sample to a slow boil, covering it with a watch glass to prevent loss of sample. Boil for 10 minutes to remove excess $H_2O_2$, then cool to room temperature. Pour into 100 milliliter volumetric flask. Wash the beaker with distilled water, pouring washes into 100 ml volumetric also. Add distilled water to bring volume up to mark.

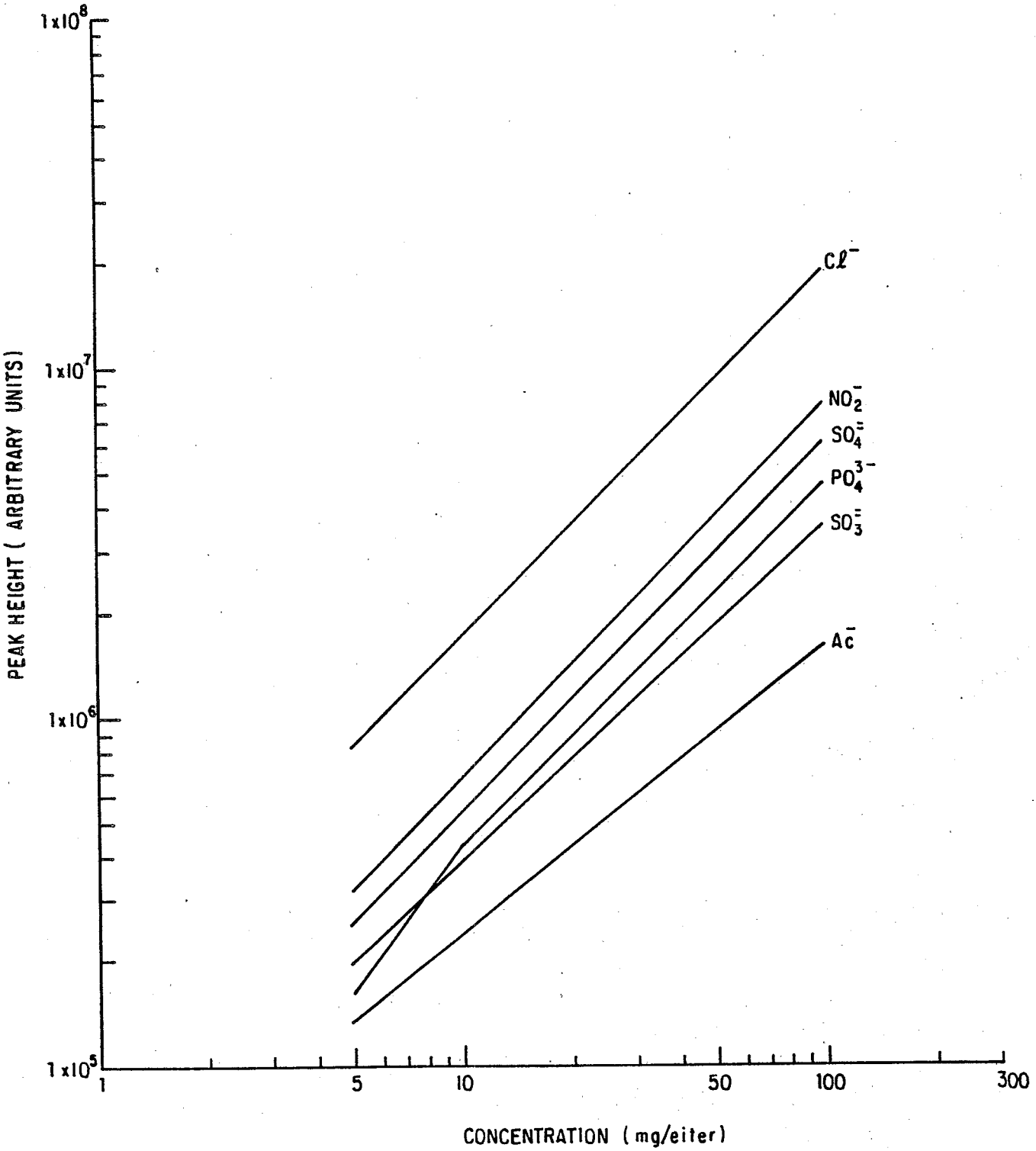


FIGURE 2-10

Calibration curves for the early eluters

Procedure

Analyze sample for sulfate using weak eluent. (See procedure for early eluters.) Correct calculated concentration for the dilution.

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## SECTION 3

## THE DETERMINATION OF SULFIDE IN OIL SHALE WASTEWATERS

As with most synthetic fuel projects, oil shale retorting produces a series of wastewaters which contain principally dissolved $CO_2$ and $NH_3$, but also numerous inorganic and organic ions. Total dissolved material may be in the range of several tens of grams per liter, presenting numerous potential problems to the analyst in terms of interferences. Present development plans for oil shale plants call for "zero discharge" of contaminated retort wastewaters, so that the retort wastewaters must be treated for internal re-use, a goal which requires the application of reliable and rapid chemical analyses of the process waters before, during, and after the various treatment and application steps.

Although sulfide is one of the species of environmental concern, the available evidence suggests that the standard methods of chemical analysis for sulfide are not appropriate for retort wastewaters, or for that matter, wastewaters from other synthetic fossil fuel processes (Wallace, 1981). For example, the iodometric method responds to any reducing agent which reacts with iodine, including the various sulfur oxides which are found in retort waters. Other possible interferences in retort water would include ammonia and unsaturated organic compounds. The methylene blue method is also subject to interferences from reducing compounds; in addition, since retort waters are generally highly colored and turbid, such colorimetric methods are generally contraindicated. Because of these interferences, methods have been developed for separating sulfide from the rest of the sample. For example, Kolthoff and Elving (1961) recommend acidifying the sample and purging the resulting $H_2S$ into a bubbler containing zinc acetate. The resulting ZnS precipitate can then

be analyzed by either standard method. Similarly, the APHA (1976) recommends separating sulfide by adding zinc acetate and removing the ZnS precipitate. Either separation method is most likely to succeed when sulfide is the only form of S present. However, for retort waters, which contain other reduced S compounds, the removal of sulfide may upset the equilibrium and produce additional sulfide. In addition, it is not clear whether these separation techniques cleanly remove potentially interfering organic compounds which may either co-distill or co-precipitate.

These difficulties may explain why Fox et al. (1978) obtained erratic results in their efforts to measure sulfide in retort water with the distillation/iodometric titration. In any case, even if distillation and precipitation procedures may be helpful in the laboratory, they are too cumbersome and time consuming for field use.

In order to avoid these problems with the standard methods, several investigators have turned to a potentiometric titration for the determination of sulfide in complex, colored, and turbid wastewaters from other sources. These methods generally involve titrating with Pb, Ag, or Cd while monitoring the precipitation with the AgS membrane electrode, although several variations have been reported in the literature.

While any titrant forming a metal sulfide precipitate could be used, the selectivity of the titration with retort wastewaters is improved by selecting a titrant which reacts only with sulfide. For a $Ag^+$ titrant, Schmidt and Punger (1971) considered a number of possible interferences, including $SCN^-$ and $S_2O_3^=$, both of which occur in retort wastewaters. The latter two species were shown to be capable of deforming the end point of the $Ag^+$ titration. Gruen and Harrap (1971) also observed that the presence of thiosulfate deformed the shape of the sulfide end point. Schwartz and Light (1970) explored the utility of

$Ag^+$ as a titrant for the determination of sulfide in wastewaters from a pulp and paper mill. Although this titrant was acceptable for pure solutions of sulfide, it did not consistently produce a sharp end point with wastewaters, presumably because of the high level of complexing and reducing organic compounds. In addition, a silver mirror was observed with some wastewaters, indicating that the $Ag^+$ had been reduced. Schwartz and Light also investigated Hg(II) as a titrant and found non-stoichiometric results, especially in the presence of dissolved $NH_3$. Florence and Farrar (1980) investigated Ag(I), Hg(II), Zn(II), Cd(II), and Pb(II) as titrants using artificial standards. Pb(II) was seen to give the most accurate result based on a stoichiometric reaction.

For these reasons, Pb(II) was selected as the titrant of choice for further evaluation. Previous authors have employed either $Pb(NO_3)_2$ or $Pb(ClO_4)_2$ which they standardized with a $Na_2H_2EDTA$ titration (Baumann, 1974; Florence and Farrar, 1980). However, Florence and Farrar also claimed that the Pb(II) titration was not quite stoichiometric, yielding a result 6% lower than would be expected based on the formation of PbS. This finding led them to standardize the Pb solution against a previously standardized sulfide solution in order to obtain the most accurate results.

Haas (1979) and Prien et al. (1977) have reported the use of the AgS electrode for the measurement of sulfide in retort wastewaters. Neither reported operational problems such as drifting or erratic results. In addition, Haas' results for sulfide agreed well with his measurements for total sulfur, a result which is reasonable for the type of retort waters which he was analyzing. On the other hand, neither author reported to have examined the possibility of interferences. Neither did they include data on the range, precision, or accuracy of their method.

The objective of the work described herein is, therefore, to rigorously determine the efficacy of the Pb(II) titration method for determining sulfide in oil shale wastewaters. Of specific concern is the effect of potential interferences from compounds which are known or suspected to occur in retort wastewaters, as well as the figures of merit such as the precision, accuracy and range of the technique. Because of many possibilities for interferences due to known and unknown species in retort wastewater, a Gran's plot method was selected for the end point determination (Gran, 1962). This method determines the equivalence point by considering several potential/volume points throughout the titration and is thus less dependent on occurrences near the equivalence point where spurious reactions are most likely to occur.

Since the proposed technique is to be used for the evaluation of pollution control systems under field conditions, it is important that the titration be sufficiently rugged to give reliable results under conditions which are less ideal than those found in the average laboratory. The method must be reliable and insensitive to environmental conditions. It also must be rapid enough to provide the plant operator with analytical data soon enough to evaluate and optimize plant operation. The ruggedness of the method under discussion has therefore been evaluated through extensive application under field conditions with actual retort water samples. Equally as important as the analytical method is the sampling and preservation technique, which also has been investigated with fresh retort waters.

EXPERIMENTAL SECTION

Pb(II) titrant was prepared from Analytical Reagent $Pb(NO_3)_2$ (Mallinckrodt, Inc.), at concentrations of 1,000 and 10,000 mg/l of Pb. Titrant was protected from $CO_2$ in the air with guard tubes containing ascarite. $NaIO_3$ was primary standard grade from Anachemia. $Na_2S_2O_3$ and starch solutions

were prepared from "Acculute" concentrates from Anachemia. All other chemicals were reagent grade or better unless otherwise indicated. Sulfide anti-oxidant buffer (SAOB) was prepared by dissolving 80 g of NaOH and 35 g of ascorbic acid in 1 liter of distilled water. Sulfide stock solution was prepared by dissolving 7.0 g of $Na_2S \cdot 9H_2O$ in 100 ml of 50% SAOB in distilled water. Sulfide standards were prepared by diluting the sulfide stock solution with 50% SAOB in water.

Electrodes were an Orion AgS membrane electrode (Model 941600) and an Orion double junction reference electrode (Model 900200) with 10% w/v $KNO_3$ in the outer chamber. During all titrations cell voltages were measured with a Keithley Model 616 digital electrometer, which for the potential range encountered could be read to ± one mV. Attempts were made to determine sulfide directly from the electrode calibration curve, for which a more precise potential measurement was required. For this purpose the potential was measured with a Data Technology Corporation Model 370 digital voltmeter connected to the analog output of the Keithley electrometer.

Titrations were carried out by placing 50 ml of sample in a stirred beaker containing 50 ml of SAOB. The electrodes were introduced into the beaker and the titrant [either 10,000 mg/l or 1,000 mg/l of Pb(II)] was selected based on the original cell potentials in order to keep the titrant volume in the range 0.5 to 10 ml.

For routine application, the cell potential and titrant volume are recorded typically three to four times during the course of the titration, and the equivalence point is determined by the Gran's plot technique (Gran, 1962), either graphically or on a desk top calculator.

Analysis under field conditions were performed at the North Site of the Laramie Energy Technology Center in support of the tests of various pilot scale pollution control systems.

RESULTS AND DISCUSSION

Original examination of the sulfide electrode indicated that it gave a linear Nernstian response over the range 1-1,000 mg/l of sulfide. The cell potential normally stabilized to within ± one mV (the limit of readability of the electrometer) within a few seconds. Response time gradually degraded when the electrode was used with retort wastewaters, but could be restored by burnishing the electrode surface according to the manufacturers instructions.

First efforts with the electrode were directed to selecting a method for determining the end point for a manual titration. For this effort, artificial sulfide standards were used to establish the shape of the titration curve, which was a typical "S"-shaped curve with a break point of approximately 200 mV. With such a large break point, it was evident that the end point could be determined by the deflection point by plotting cell potential, E, vs added volume. However, this approach proved to be tedious, requiring the careful addition of titrant near the end point and the plotting of several data points.

Rather than plotting the data, an attempt was made to determine the end point by monitoring the cell potential with an analog meter and observing the sudden change in cell potential. This approach proved to be less reproducible than plotting the data.

Finally, a Gran's plot method was tested and proved to be the most convenient for use with a manual titration. (The Gran's plot method permits the analyst to collect several data points, each consisting of a cell potential and volume of added titrant, throughout the midrange of the titration. The volumes added are otherwise arbitrary, and special care is not required near

the end point.) For this reason, and for the reasons discussed in the introduction, the Gran's plot technique was used for the rest of this investigation. However, since either the deflection point technique or the Gran's plot technique gave equivalent results, it might be possible to use the former technique for an automated titrator, many of which use derivative techniques for end point determination.

Three different variations of the Gran's plot method, each of which give equivalent results but differ in ease of use, were used throughout this investigation. The first variation used the traditional Gran's plot paper (Orion). This approach required a supply of specialized paper which was not always readily available, and also lacked the resolution which was sometimes helpful in achieving the most precise results.

For the second approach the fraction, f, of the sulfide which had been titrated was calculated at several points throughout the titration from the expression:

(1) $$f = \frac{V_o + V_t}{V_o} 10^{(E-E_o)/m}$$

where $V_o$ = total volume in titration vessel at start of titration
$V_t$ = volume of titrant added
$E_o$ = starting cell potential
$E$ = cell potential
$m$ = Nernstian slope

The fraction f was then plotted against the volume of titrant added, resulting in a straight line with an intercept equal to the equivalent volume. The third variation was completed entirely with a Hewlett Packard model 9825A calculator, which calculated the fraction f at each data point, fit a least squares line to the data pairs, and then calculated the end point and sample concentration. (This program is listed in the Protocol section.) Data corresponding to

$0.05<f<0.95$ were rejected by the program prior to the calculation in order to emphasize the midpoints of the titration.

The next step in this investigation was to establish the accuracy of the titration by comparison to an independent method which was traceable to a primary reference compound. For this purpose, pure solutions of $Na_2S$ were analyzed by both the titration described in this paper and the standard iodometric titration (APHA, 1976). Accurately known concentrations of $I_3^-$ were prepared by adding primary standard grade $KIO_3$ to a solution of KI according to the reaction:

(2) $$8I^- + IO_3^- + 6H^+ \rightarrow 3I_3^- + 3H_2O$$

The thiosulfate solution was then standardized by titration into this solution, according to the following reaction:

(3) $$I_3^- + 2S_2O_3^= \rightarrow 3I^- + S_4O_6^=$$

To determine sulfide an aliquot of sample was added to a solution containing an excess of $I_3^-$:

(4) $$S^= + I_3^- \rightarrow 3I^- + S^o$$

Excess $I_3^-$ was determined by titration with thiosulfate to a starch end point, and sulfide was calculated by difference. Since both $I_3^-$ and thiosulfate concentrations are traceable to a primary reference standard, the sulfide is similarly traceable. Replicate analyses by the iodometric and lead titration methods yielded results of 2,309 and 2,322 mg/l, respectively. Since the precision of the lead titration is approximately ± one percent, there is no significant difference in these results, and it can be concluded that the lead titration method is accurate for pure solutions of sulfide at concentrations of approximately 1,000 mg/l.

In order to establish the working range of the method, a series of artificial standards was prepared and analyzed. The results of these analyses

are shown in Table 3-1, where the "simple" matrix refers to standards prepared in SAOB and the "complex" matrix is discussed below. For the data in this table the recovery of the 967 mg/l sample was set equal to 100%, based on the results of the last paragraph, and the remaining recoveries were calculated therefrom. The recoveries for one and five mg/l samples differ slightly from 100%. While the statistical interpretation of this data is discussed in more detail in Appendix 3A, suffice it to say at this point that the significance of the difference is marginal for the 5.8 mg/l sample but is substantial for the 0.967 mg/l sample. These data suggest that recovery of the titration is approximately 10% low at 1 mg/l, and possibly 3% low at 5 mg/l. Similar results have been observed by Florence and Farrar (1980) for low level sulfide titrations. However, from the data available it is not clear whether the titration actually yields low results at the mg/l level or the sulfide standard is slightly lower than expected, perhaps due to partial oxidation. Thus, the data in Table 3-1 imply that the accuracy of the titration is at least 97% at the five mg/l level and at least 87% at the one mg/l level. As discussed in the previous paragraph, the accuracy is essentially 100% at higher levels.

For the purposes of wastewater treatment in the oil shale industry, there is little importance in determining sulfide below one mg/l, since the water is destined for internal re-use rather than discharge. In fact, most samples encountered by the authors during the operation of pilot-scale wastewater treatment plants at oil shale facilities contain over 100 mg/l sulfide. Referring to Table 3-1, it is apparent that the results for the 5.8 and 0.967 mg/l samples are both within 0.2 mg/l of the expected value, which is sufficiently close to satisfy this purpose. However, titrations below one mg/l should be approached with caution.

Table 3-1

RECOVERY OF SULFIDE AT VARIOUS CONCENTRATIONS AND IN VARIOUS MATRICES

| Sample Number | Matrix | Expected Sulfide Concentration (mg/l) | Measured Sulfide Concentrations (mg/l) | Average Measured Sulfide Concentration (mg/l) | Recovery** (%) |
|---|---|---|---|---|---|
| 1 | Simple | 967 | 965, 984, 953 | 967 ± 9* | 100 ± 1 |
| 2 | Simple | 5.80 | 5.66, 5.59, 5.67 | 6.64 ± .03 | 97.2 ± 1 |
| 3 | Simple | 0.967 | 0.867, 0.853, 0.825 | 0.848 ± .01 | 87.7 ± 1 |
| 4 | Complex | 967 | 950, 1000, 949 | 966 ± 17 | 100 ± 1 |
| 5 | Complex | 5.80 | 5.78, 5.73, 5.69 | 5.73 ± .03 | 98.8 ± 1 |
| 6 | Complex | 0.967 | 0.878, 0.879, 0.899 | 0.885 ± .01 | 91.5 ± 1 |

* The error limits shown are one standard deviation of the average based on the three samples shown.

** Recovery = (average measured concentration)/(expected concentration). The error limits are for the average value, as discussed in Appendix 3A.

Before the titration procedure can be applied to retort waters consideration must be given to the potential interfering effects of the many compounds in retort water. While it is not possible to prepare artificial standards containing all compounds found in retort water, major components can be added to solutions containing known amounts of sulfide. For this purpose, sulfide standards were prepared containing 1-1,000 mg/l sulfide in addition to the following levels of possible interfering compounds: $SCN^-$, $S_2O_3^=$, $SO_4^=$, $Cl^-$, and $CO_3^=$ at a concentration of 1,000 mg/l were added as their sodium salts; 68.0 g/l of $(NH_4)_2CO_3$; and 40 g/l of NaOH to neutralize $NH_4^+$ during titration.

The results of the addition of the possible interfering compounds is seen in Table 3-1 by comparing the results obtained for the "complex" samples with those obtained for the "simple" samples with the same sulfide concentration. Any interference occurs only in the low level sulfide and at levels of only a few percent. All errors due to interferences are less than 0.1 mg/l for the low level samples and are not measurable at the higher levels of sulfide. Concentrations of possible interfering compounds in the samples under consideration are larger than normally encountered in the authors' laboratory, and this implies that errors due to these added compounds are not significant in regard to the treatment of retort waters. However, for application of this technique to other wastewaters where low level measurements are more important, it should be noted that the results for samples 3 and 6 are statistically different at the 95% confidence level. It is therefore recommended that application of this technique to samples containing less than one mg/l be preceeded by additional investigation of possible interferences.

At this time the titration method has been applied to retort wastewaters in support of tests of various pollution control systems, including venturi scrubbers, steam strippers, and reverse osmosis units; results have been very

encouraging. Precision of the method when applied to the routine analysis of retort waters containing sulfide in the range of 1-1,000 mg/l is typically 2-3% relative or ± 0.1 mg/l. The contribution of the electrometer to this level of precision was examined as follows: a Gran's plot calculation was first carried out on a set of titrant volumes and cell potentials which were artifically selected so as to be exactly consistent, that is, to yield an exactly straight line when plotted on Gran's plot graph paper. Next, the same calculation was repeated after altering a potential by small increments while leaving all other parameters unchanged. This procedure resulted in a variation of approximately 2-3% in the calculated sulfide concentration for errors of one mV in the cell potential. Since the electrometer used for the field measurements was readable to only ± one mV, it appears likely that the readibility of the electrometer was a major contributor to the imprecision of the method. These data also suggest that using an electrometer capable of reporting to ± 0.1 mV could improve the precision if that should be needed. The recovery as measured by adding known amounts of sulfide to the sample is 100% within the precision of the method.

The titration can be carried out routinely with a minimum of equipment, and has caused few problems. The only difficulty encountered has been with samples from a steam stripper which contained less than a few mg/l of sulfide, for which a drifting electrode potential was sometimes observed. This made the titration more difficult. In order to compensate for such drift, the titration was performed more rapidly than usual with apparently no ill effects and results were reported only to the closest one mg/l.

Although in theory the titration can be completed without ever calibrating the AgS electrode, it is helpful to carry out a calibration occasionally, perhaps every few weeks. When this is done, the calibration is stable enough

to permit selection of a titrant of proper strength by observing the cell potential at the start of the titration, and to thereby avoid titrating the same sample twice. Order-of-magnitude agreement between the concentrations indicated by the titration and cell potential assures against mistakenly titrating a non-sulfide species, such as $CO_3^{=}$, when sulfide is absent. An occasional calibration is also helpful in checking for proper electrode response.

Preparation of standards from solid $Na_2S \cdot H_2O$ in a field laboratory is usually inconvenient and standards are not sufficiently stable to allow for advance preparation and storage in polyethylene containers. Concentrated standards (11,000 mg/l) were therefore prepared and sealed in 20 ml, pre-scored glass vials which are sealed by melting an elongated glass neck. Before sealing, the head space but not the liquid in the vial, was flushed with $N_2$. It was hoped that by hermetically sealing the container and by using concentrated solutions, standards would be stable indefinitely. In the field laboratory standards could be prepared simply by diluting the contents of the vial. Measurements of solutions stored in vials showed no measurable decay over a 9 month period. The use of standard concentrates in hermetically-sealed glass containers is thus a promising method for storing sulfide standards.

Performing the titration technique on site during various field tests has made it possible to examine the stability of sulfide in fresh retort wastewaters. During normal operation, samples designated for sulfide analysis are buffered with 50% SAOB immediately upon collection and are analyzed within one hour. Select samples were set aside for sulfide time decay measurements. Samples which were filtered through a 0.45 micrometer filter and stored at 4°C in tightly sealed polyethylene bottles were observed to lose approximately 20% of their sulfide content per day and to be essentially free of sulfide in two

weeks. In a separate test, fresh retort wastewaters stored at room temperatures in similar containers lost 99% of the sulfide within 24 hours. Samples stored in SAOB were more stable, losing approximately 20% in 10 days, mostly in the first two days. While an insufficient number of samples have been examined to draw any conclusions regarding the typical decay rate of sulfide, it is clear that samples must be analyzed immediately upon collection to assure a realistic sulfide measurement.

If retort waters are analyzed promptly upon collection, it is observed that sulfide is the major form of sulfur present. In comparison, several other investigators, who did not have access to fresh retort waters, have reported that the major species in retort water are $S_2O_3^{=}$, $SO_4^{=}$, and $SCN^-$ (Stuber et al., 1978). However, based on the data observed in this study it appears likely that the latter species arise, at least in part, from the oxidation of sulfide during storage rather than being an original component in retort water.

Finally, the titration method was compared to the direct calibration technique as a method for measuring sulfide in retort wastewater. That is, does the potential from the AgS electrode give an adequate measurement of sulfide, assuming the electrode to be calibrated with sulfide standards? If so, the direct calibration technique would be an attractive basis for a continuous-flow, automated analyzer.

Under normal laboratory conditions it was observed that the electrode potential would vary approximately 3 mV when immersed in a series of solutions, each containing the same sulfide concentration. For the sulfide electrode 3 mV corresponds to an error of approximately 23%, and an effort was therefore made to define and minimize the sources of this drift. Since temperature variations are one possible source of error, a series of identical samples was analyzed

over the range of 20-30°C. No effort was made to control the temperature of the un-immersed part of the electrode, so that temperature gradients were likely. Under these conditions, a temperature change of 1°C caused a 2% error in the concentration measured. Changing the ionic strength of the solution by approximately one mole/l also caused the measured sulfide concentration to vary by a few percent. Although all sources of error were not identified in this limited effort, it appeared that best results could be obtained by controlling both the temperature and ionic strength of samples and standards.

The principal difficulty with using the direct calibration technique was the need for frequent calibration with sulfide standards. This difficulty was compounded because the sulfide standards are unstable and require frequent preparation. In the final analysis, the direct calibration technique proved too time consuming and difficult for routine application, although it has been used in applications requiring a continuous monitor. In comparison, the Pb titration is especially attractive because the titrant is stable indefinitely, thereby contributing to its reliability.

CONCLUSIONS

The titration with Pb(II) using an AgS electrode as an indicator and a Gran's plot procedure to determine the end point is an acceptable method for measuring sulfide in retort wastewaters over the range 1-1,000 mg/l. Significant interferences have not been found. The precision of the technique with retort wastewaters, as applied during routine monitoring, is typically 2-3% relative or ± 0.1 mg/l, whichever is greater. The data suggest that samples containing one mg/l give results approximately 0.1 mg/l lower than expected. No bias is observed at higher concentrations, and the accuracy of the method is therefore limited only by the precision for samples containing more than 5 mg/l of sulfide. The titration has proven reliable, simple, and

rapid when applied under field conditions. The titration method as described in this text is thus attractive as a reference method for the measurement of sulfide in retort wastewaters.

In comparison to the titration method, the direct calibration curve method is less accurate and precise for routine use with a variety of samples, but may be appropriate for monitoring a series of similar samples under closely controlled conditions of temperature and ionic strength. The main advantages of the direct calibration curve technique are that it requires only a single measurement for each sample and it can be applied as a monitor in a continuous flow system. However, these advantages are more than offset by the lesser accuracy and reliability of the direct calibration method. In addition, the direct calibration method requires frequent calibration with unstable standards, while the titrant for the titration method is stable indefinitely.

Concentrated sulfide standards have been shown to be stable when stored in SAOB in hermetically sealed vials for periods up to 9 months. This approach is suggested as a possible means of providing sulfide standards to field laboratories.

RECOMMENDED METHOD FOR TOTAL SULFIDE IN RETORT WASTEWATERS

Principle

Sulfide is titrated with Pb(II) using the AgS ion selective electrode as an indicator. The end point is determined by a Gran's plot technique.

Reagents

1. Sulfide Anti-Oxidant Buffer (SAOB). (50 ml/sample)

   In a 1 liter volumetric flask place 600 ml distilled water, 80 g NaOH (or 175 ml of 33% w/w NaOH), and 35 g ascorbic acid. Dissolve and bring to volume.

2. 10 M NaOH. (0-10 ml/sample)

   Dissolve 40 g NaOH in 100 ml volumetric flask. Dilute to volume. This is needed only to check electrode performance and not for routine work.

3. Pb stock solution. (10,000 mg/l as Pb)

   Add 15.985 g Analytical Reagent grade $Pb(NO_3)_2$ to a 1 liter flask. Dissolve and bring to volume.

   $$(Pb) = (0.6256)x[\text{mass } Pb(NO_3)_2]$$

4. Pb titrant. (1-10 ml/sample)

   Dilute the Pb stock solution 10:1 volumetrically, or as needed to arrive at a titrant volume of 1-10 ml.

5. $S^=$ Stock Solution (10,000 mg/l.)

   Add 7.49 g of AR grade $Na_2S \cdot 9H_2O$ to a 100 ml volumetric flask. Add 50 ml SAOB and bring to volume with de-oxygenated, d.i. $H_2O$.

   $$(S^=) = 0.1335 \text{ X } Na_2S \cdot 9H_2O$$

   This is needed only to check electrode performance and not for routine work.

6. Standard $S^=$ Solutions. (needed only to check electrode)

   Dilute the $S^=$ stock solution with 50% SAOB in distilled $H_2O$.

<u>Equipment</u>

1. 2 burets, 10 ml each
2. 250 ml beakers, 1 per sample
3. pH electrode and meter
4. AgS ion selective electrode (Orion)
5. Double junction reference electrode with an inner filling solution from manufacturer and an outer filling solution of 10% w/v $KNO_3$

6. electrometer, capable of reading 800 mV to the nearest mV

7. 10 ml graduated pipet (optional)

8. 50 ml dispenser for SAOB

Procedure

The procedure as described below is applicable to waters containing sulfide in the range 1-310 mg/l, and minor adjustments must be made for more concentrated samples. For samples containing more than 310 mg/l it is convenient to reduce the sample volume in order to keep the titrant volume within 10 ml. Similarly, for samples containing unusually large amounts of $NH_4^+$ and $HCO_3^-$ (approaching one m/l) it is recommended that additional base be added in the form of 10 M NaOH. The function of the additional base is to convert the $H_2S$ and $HS^-$ to $S^=$, which requires a pH of approximately 14. However, excessive amounts of $NH_4^+$ and $HCO_3^-$ buffer the solution and prevent this pH from being attained.

The following procedure is divided into protocols which should be performed occasionally, perhaps every few weeks and during the initial set up, and protocols which should be performed during each analysis. Performing a calibration of the electrode every few weeks is normally sufficient to permit the analyst to estimate the concentration based on the original electrode reading, and thereby to select the titrant of proper strength.

Procedures to be Performed Occasionally--

Standardize the electrode. Standardize the stock sulfide solution by titrating with Pb(II) as described below. Prepare sulfide standards by volumetric dilution in 50% SAOB covering the range 1-1,000 mg/l. Into a 250 ml beaker, place 50 ml of SAOB and 50 ml of standard solution. Place the beaker on a magnetic stirrer, immerse the electrodes, and record the potential. Plot potential vs concentration on semi-log paper. The resulting calibration curve

should be straight with a slope close to 30 mV per decade change in concentration.

NaOH requirement for concentrated samples. Add 50 ml of SAOB and 50 ml of sample to a 250 ml beaker. Add a magnetic stirrer and insert the AgS electrode, the reference electrode, and a pH electrode. The pH should be close to 14. If it is not, adjust with 10 M NaOH, until the pH is 14 or until the potential of the sulfide electrode stabilizes within a few mV. Note the volume of NaOH required and add the equivalent amount to samples containing similar concentration of $NH_4^+$ or $CO_3^=$.

Drifting electrode response. During the analysis of retort waters, the AgS electrode often develops a slow and drifting response after a few days use. A more rapid response can normally be restored by burnishing the electrode as described by the manufacturer.

Procedures to be Performed With Each Sample--

Immediately upon collection add 50 ml of sample to 50 ml of SAOB in a 250 ml beaker. Place on a magnetic stirrer. This solution may remain in a covered beaker for up to an hour before titration although immediate analysis is preferred. Do not allow the sample to stand after collection without the addition of SAOB.

Place the beaker on a magnetic stirrer, begin stirring, and insert the AgS and reference electrode. Based on the original cell potential, select a titrant which will result in a titrant volume of 1-10 ml. Gradually add titrant with stirring. (A black precipitate is evident immediately after the addition of titrant unless the sample is opaque.) Stop adding the titrant at several locations and record the buret reading and cell potential. Four readings spaced in the range $2<(E-E_0)<35$ mV are normally an adequate number of data points.

Recording Data

The following data must be recorded in order to calculate the sulfide concentration:

Once per Sample

$E_o$ = original potential in mV

$V_o$ = total volume in beaker (SAOB + sample)

$V_{start}$ = starting buret reading

(Pb) = titrant concentration

$V_{sample}$ = volume of sample

At each stopping point

E = cell potential in mV

$V_B$ = buret reading

Calculations

Determine the equivalence point, $V_{eq}$ using Gran's Plot Paper or by plotting the function:

$$f = \frac{V_t+V_o}{V_o} 10^{(E-E_o)/m}$$

Where $V_t$ = titrant volume
$m$ = Nernstian slope from the calibration curve = 29.5 mV at 25°C

Calculate the sulfide concentration from the equation:

$$(S^=) = V_{eq} \cdot (Pb) \frac{0.1548}{V_{sample}}$$

Where (Pb) is the lead concentration in mg/l and $V_{eq}$ is the equivalence point.

Alternately, the calculations can be performed automatically by the following program designed to operate on a Hewlett Packard Model 9825 calculator. This program performs a least squares fit of the function f to a straight line and thereby determines the $V_{eq}$ and the sulfide concentration.

Values of f>0.95 and <0.05 are rejected, so that at least two measurements are required which give values of f in the range 0.05 to 0.95. This normally corresponds to changes in the cell potential in the range 1 to 35 mV.

Instructions for Gran's Plot Program

1. If the 9825 is off, insert the tape cartridge and turn it on.

   If the 9825 is on, but the program is not loaded, insert the tape cartridge and type '1dp 0 EXECUTE', where everything inside the quotes is typed and EXECUTE means press the key marked EXECUTE.

   If the 9825 is on and the program is loaded, just type 'RUN'.

2. If the calculator beeps and displays "error nn", where nn are numbers or letters, start again. If it happens again, consult the manual.

3. The program should be running and displaying the first prompt.

4. The following data are entered once for similar sample conditions:

   Date (mm/dd/yy) - maximum of 8 characters

   Log coefficient (29.5 or other)

   $V_0$ - displayed as "V(0)"

   $V_{sample}$ - displayed as "V(sample)"

   Pb concentration

5. For each sample the following items are requested:

   Sample ID - maximum of 16 characters

   $E_0$ - displayed as E(0)

   Starting buret reading

6. Enter the data points for the sample:

   E and $V_t$ (buret reading), these will be printed. Continue until there are no more, then just press 'CONTINUE' when asked for the next value of E.

7. Make any needed corrections. When asked "Remove data (y/n)?", type 'y' or 'CONTINUE' for yes, 'n' for no. If no, go to Step 8.

   If you wish to remove data, the prompts are in the same order as for entering data. When you have removed all the points you wish, just press 'CONTINUE'.

   After removing data, you will be asked "Enter more data (y/n)?". If you wish to enter corrected data points, type 'y' or 'CONTINUE' for yes, 'n' for no. If yes, go to Step 6.

8. The results will be printed. $V_{eq}$ is the equivalent volume, Cs is the calculated sample concentration and R is the correlation coefficient.

9. If for the next sample, the data entered in Step 4 is the same, go to Step 5.

   If the data in Step 4 should be different, press 'STOP' and then press 'RUN' and go to Step 4.

Table 3-2

GRAN'S PLOT OUTLINE

```
0:  "Sulfide concentration":gto "start"
1:  "f":ret (V+T)tn^((E-C)/G)/V
2:  "Cs":ret HP(.1548/8)
3:  "yes":ret flg13 or cap(Y$[1,1])="Y"
4:  "sum":
5:  S[1]+p3p1→S[1]
6:  S[2]+p3p2→S[2]
7:  S[3]+p3p1p1→S[3]
8:  S[4]+p3p2p2→S[4]
9:  S[5]+p3p1p2→S[5]
10: N+p3→N;it N>=0;ret
11: beep;dsp "Too many points removed.";end
12: "regress":
13: S[1]/N→X
14: S[2]/N→Y
15: (S[3]-NXX)/(N-1)→L
16: (S[4]-NYY)/(N-1)→M
17: (S[5]-NXY)/L(N-1)→B
18: Y-BX→A
19: -A/B→H
20: B√(L/M)→R
21: ret
22: "ent_data":
23: prt "Entered data:","E","V(t)"
24: ent E; if flg13;ret
25: ENT "Burette reading?",Z
26: if flg13;gto -1
27: Z-D→T;prt E,Z;spc
28: 'f'(E,T)→F
29: if F>.05;cll 'sum'(T,F,1)
30: if F>.05 and F<.95;cll 'sum'(T,F,1)
31: gto -7
32: "rmv_data":
33: prt "Removed data:","E","V(t)"
34: ent E; if flg13;ret
35: ent "Burette reading?",Z
36: if flg13;gto -1
37: Z-D→T;prt E,Z;spc
38: 'f'(E,T)→F
39: if F>.05;cll 'sum'(T,F,-1)
40: if F>.05 and F<.95;cll 'sum'(T,F,-1)
41: gto -7
42: "get_data":
43: cll 'ent_data'
44: ent "Remove data(y/n)?",Y$
45: if not 'yes';ret
46: cll 'rmv_data'
47: ent "Enter more data(y/n)?",Y$
48: if 'yes';gto -5
49: ret
```

Table 3-2 (cont.)

```
50: "prt_hdr":
51: spc 2;wrt 16.1
52: prt "Sample:",I$
53: prt "Date:",D$
54: spc
55: wrt 16.2,G;wrt 16.3,C;wrt 16.4,V
56: wrt 16.5,J;wrt 16.6,P;wrt 16.7,D
57: spc ;ret
58: "prt results":
59:
60:
61: fxd 5;prt "R:",R
62: wrt 16.1
63: spc 3;fxd 2;ret
64: "get_info":
65: ent "Date(mm/dd/yy)?",D$
66: ent "Log coeff?",G;if flg13;gto +0
67: ent "V(0)?",V;if flg13;gto +0
68: ent "V(sample)?",U;if flg13;gto +0
69: ent "Pb conc?",P;if flg13;gto +0
70: ret
71: "get_smpinfo":
72: ent "Sample ID?",I$
73: ent "E(0)?",C;if flg13;gto +0
74: ent "Starting burette reading?",D;if flg13;gto +0
75: ret
76: "mem_init":
77: dim D$[8],I$[16],S[5],Y$[6]
78: fmt 1,16"-"
79: fmt 2,"Log coef:",f7.2
80: fmt 3,"E(0):",f11.2
81: fmt 4,"V(0):",f11.2
82: fmt 5,"V(smpl):",f8.2
83: fmt 6,"Pb conc:",f8.2
84: fmt 7,"Bur start:",f6.2
85: fmt 8,"Veg:",f12.2
86: fmt 9,"Cs:",f13.2
87: 0→N;fxd 2
88: ret
89: "0→S[*]":0→S[1]→S[2]→S[3]→S[4]→S[5]→N;ret
90: "start":
91: cll 'mem_init'
92: cll 'get_info'
93: cll 'get_smpinfo'
94: cll '0→S[*]'
95: cll 'prt_hdr'
96: cll 'get_data'
97: cll 'regress'
98: cll 'prt_results'
99: gto -6
*30484
```

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## APPENDIX 3A

## STATISTICAL INTERPRETATION

This section describes the application of the "t" test to the data in Table 3-1. First, consider the standard deviation which should be associated with each recovery. In theory the uncertainty in the recovery, as a quotient of two numbers, should depend on the uncertainty in both the "measured" and "expected" concentrations (Table 3-1). However, the uncertainty in the latter can be neglected since volumetric dilution errors are insignificant in comparison to the errors associated with the titration, and the standard deviation of the recovery can therefore be obtained simply by dividing the standard deviations in Column 4 by the expected concentrations.

While this calculation yields the standard deviation based on a set of three analyses, a more precise estimate of the standard deviation can be obtained by averaging all standard deviations in Column 4 of the table, as follows:

(A1)
$$s_j^2 = \frac{R_j^2}{6}\left[\frac{s^2(\bar{x}_1)}{\bar{x}_1^2} + \frac{s^2(\bar{x}_2)}{\bar{x}_2^2} \cdot \cdot \cdot \frac{s^2(\bar{x}_6)}{\bar{x}_6^2}\right]$$

where $s_j^2$ = variance of the recovery for the $j^{th}$ sample

$s^2(\bar{x}_i)$ = variance of the average for the $i^{th}$ sample set

$\bar{x}_i$ = average concentration for the $i^{th}$ sample

$R_j$ = recovery for the $j$th sample

Carrying out this calculation yields an estimated standard deviation of 0.011 for the recovery for all samples. (This value is reasonable in view of the typical precision obtained with this analysis during routine application.)

Determining whether the recoveries differ from unity, or from each other, thus requires application of the t test to the recoveries in Column 5 (Volk, 1969).

To determine whether the recoveries, R, differ from unity, t is calculated from the expression:

$$t = \frac{R - 1.00}{0.011 \sqrt{2}} \quad \text{(A2)}$$

Referring to tables of the t distribution indicates that the recovery of the 5.80 mg/l pure sample differs from unity with a 90% probability (t = 1.8). That is, if the recovery is actually 1.00, the probability is 10% that $t \geq 1.8$. For the 0.848 mg/l pure sample (Sample 3), t = 7.9, and the recovery is not equal to unity with a 99.9% probability.

The effect of interferences can be measured by calculating the t value for sample pairs i and j:

$$t = \frac{R_i - R_j}{0.011 \sqrt{2}} \quad \text{(A3)}$$

Obviously, no measureable interference occurs at a sulfide concentration of 1,000 mg/l (Samples 1 and 4). For the 5.80 mg/l samples, t = 1.0, also not large enough to conclude that an interference exists. At 0.967 mg/l (sample pair 3 and 6), t = 2.4, a value that would be exceeded in 5% of the cases if no interference existed. It thus appears that the results for Samples 3 and 6 are thus (barely) significantly different.

## SECTION 4

## TOTAL SOLUTES IN RETORT WASTEWATERS

The measurement of total residue, which is defined as the mass remaining when a sample is dried at 103-105°C, is performed frequently on ground and surface waters to determine total solutes in the sample (EPA, 1979). Unfortunately, many major components of retort waters, most notably carbonate, bicarbonate, ammonia, and volatile organic compounds, are lost during the drying process. The traditional residue measurement, therefore, is not normally meaningful when applied to retort wastewaters. Nevertheless, a measure of the total solute content is still important to both the wastewater engineer--who needs a simple indication of the overall effect of a treatment process--and to the analyst--who needs a quality control check for individual determinations. An alternate technique is therefore clearly desirable.

One alternative method considered in this study, as well as by other investigators, is lyophilization (freeze drying), whereby the sample remains cold throughout the drying process, only reaching room temperature (at maximum) at the moment of total desiccation. The residue is then weighed as an indication of dissolved residue.

It is widely known that for ideal solutions the colligative properties, such as boiling point elevation, freezing point depression, and osmotic pressure, are an indication of total solute content. Unlike the drying procedures commonly used for residue measurements, the colligative properties are related to total molality rather than to dissolved mass. Nevertheless, total molality provides the wastewater engineer with a gross indicator of treatment progress, and therefore can serve much the same purpose as the traditional "TDS" measurement. Similarly, total molality provides a quality

control check for the analyst, since the individual components should sum to the total molal strength, providing that the major components have been measured correctly. Thus, if the colligative properties of retort wastewaters could be measured and related to total solute strength, they would fill much the same role as the total residue measurement.

This chapter describes efforts to investigate both lyophilization and the measurement of colligative properties as an indication of total solute content. The objective of the work described below is to develop a method for measuring total dissolved material in retort wastewaters which is simple and rugged enough to be performed in a field laboratory in support of pollution control tests. The analysis should also be rapid enough to provide timely and pertinent data to the pollution control plant operator. To be of most value, the technique developed also should be applicable to other synfuel wastewaters, most of which contain similar major components as oil shale retort waters.

EXPERIMENTAL SECTION

Standards of known osmolality (osmotic strength) were prepared from "Baker Analyzed" reagent-grade NaCl dissolved in de-ionized, distilled water. Solutions of $NH_4HCO_3/NH_3$ were prepared from reagent grade ammonium hydroxide (Fisher Scientific) and analytical reagent $NH_4HCO_3$ (Mallinckrodt). The ammonium hydroxide was standardized by titration with 0.1 N $H_2SO_4$ prepared from Acculute concentrated standards using a pH meter to monitor the progress of the titration. For this titration the pH at the equivalence point varies with the concentration, a factor which was taken into account.

Retort waters of various types were obtained from the Laramie Energy Technology Center (DOE), mainly in conjunction with operations at their North Site Facility.

Selected retort water samples were analyzed on a Digimatic Model 3DII (Advanced Instruments, Inc.) to establish repeatability with retort waters. This instrument operates by automatically determining the freezing point depression of a sample. Additional freezing point depression measurements, including those listed in Table 4-1, were obtained on a Knauer manually operated cryoscope operated according to the manufacturer's instructions. Samples were stored at 4°C from preparation until analysis.

RESULTS AND CONCLUSIONS

Various retort water samples were analyzed for total dissolved residue using the standard drying technique at 103°C. As expected, residue measured by this procedure was only a small fraction of that expected based on analysis of the individual components. Lyophilization of retort waters gave similar results, implying that the ammonium carbonates also evaporate under cooled, low temperature conditions. To confirm this implication, solutions of ammonium bicarbonate and ammonium carbonate were evaporated using both lyophilization and thermal drying. With either procedure over 98% of the dissolved material was lost. It is thus clear that neither lyophilization nor thermal drying, as carried out in this experiment, are appropriate for retort wastewaters.

It is natural to ask at this point whether lyophilization carried out at a different temperature would more selectively evaporate water in comparison to the dissolved material. The answer to this question can be found by examining the vapor pressures of water and the major constituents in retort water as a function of temperature. Application of simple thermodynamic formulae indicates that the vapor pressure of ammonium bicarbonate, one of the major components of retort waters, exceeds the vapor pressure of water at all temperatures above approximately -10°C, corresponding to 0.003 atm. In theory, then, lyophilization carried out well below -10°C could selectively evaporate

Table 4-1

TOTAL SOLUTE BY FREEZING POINT DEPRESSION

| Sample | Ideal Osmolality (moles/l) | Measured Osmolality | NaCl Equivalent (moles/l) |
|---|---|---|---|
| 1.0 M $NH_4HCO_3$ + 0.1 M $NH_4OH$ | 2.1 | 1.90 | 2.0 |
| 0.1 M $NH_4HCO_3$ + 0.01 M $NH_4OH$ | 0.21 | 0.216 | 0.21 |
| 0.01 M $NH_4HCO_3$ + 0.001 M $NH_4OH$ | 0.021 | 0.021 | 0.021 |
| 1.0 M $NH_4HCO_3$ + 0.1 M $NH_4OH$ + 0.921 M. Acetone | 3.02 | 2.64 | 2.8 |
| Omega-9 Retort Water | - | 0.58 | |

water from retort water samples. However, because the vapors pressure of most organic compounds are less affected by temperature than is water, as the temperature is lowered the organic compounds in retort water would be more selectively evaporated than they are at 103°C. It thus appears that evaporation techniques, regardless of the temperature under which they are carried out, are inappropriate for retort wastewater.

The most common colligative properties for measuring total solute content include osmotic pressure, boiling point elevation, and freezing point depression. The first of these requires a semi-permeable membrane capable of passing water but not the dissolved materials. In the case of retort wastewaters, the membrane must be impermeable to both ammonia and carbon dioxide, as well as additional organic compounds. Most membranes are permeable to both these gases, and for this reason osmotic pressure was not examined.

The depression of the dew point, which is equivalent to the elevation of the boiling point, can be measured by commercially-available instruments, one of which was evaluated using NaCl standards, $NH_3/NH_4HCO_3$ standards, and retort waters. While the NaCl standards yielded reasonable results, no meaningful numbers could be obtained with the other samples. In retrospect, this result is reasonable since the proportionality between dew point depression and solute content can only be expected for non-volatile solutes (Lewis and Randall, 1961). Hence, dew point depression (and boiling point elevation) are inappropriate methods for measuring solute content of retort wastewaters.

Freezing point depression also has been evaluated using both artificial standards and actual retort waters and has proven to be the best method of those tested. Table 4-1 illustrates the application of this technique to real and simulated retort waters. In this table ideal osmolality refers to the number of moles of solute added, counting each ion separately. Measured

osmolality is the freezing point depression in °C divided by 1.86°C, the freezing point depression per mole at infinite dilution. The measured and ideal osmolality will agree to the extent that the sample behaves like an ideal (i.e., infinitely dilute) solution. The measured osmolality is sufficiently close to the actual molal strength for most field applications. The final column in the table shows the concentration of NaCl which gives the same freezing point depression as the solution under test. Comparing the data in columns 2 and 4 in this table suggests that the "NaCl equivalent molarity" is a slightly better indication of total solute content than is the measured osmolality. The measured osmolality of the retort water listed in Table 4-1 is also reasonable in view of published data on this sample (Fox et al., 1978). In conclusion, data in Table 4-1 indicate that total solute content in retort waters can be measured to an accuracy of 7% relative at concentrations up to 3 moles/l. At higher concentrations, solution non-ideality may become increasingly important, and the freezing point method is therefore not recommended for such samples. The accuracy of most devices for measuring freezing point depression is typically ±0.001 moles/l, which therefore constitutes the lower limit of this technique.

For the purpose of checking the total of the individual analyses, the data in Table 4-1 suggest that the "NaCl equivalent molarity" is the better measure. Since most species are determined in units of mg/l, they can be easily converted to moles/l and compared directly to the "NaCl equivalent". This approach may prove to be difficult with waters containing high levels of total organic carbon (TOC) which are not analyzed for individual organic species. In this case the TOC measurement cannot be related directly to molarity. However, in the author's limited experience in applying the freezing point method, the organic fraction did not appear to constitute a large molar fraction. In any

case, a high molar organic content suggests that at least the major organic species should be determined.

Repeatability of the freezing point method was determined by analyzing a variety of retort waters with the commercially available instrument listed in the experimental section of this report. Most results could be repeated to within ±0.001 osmols, indicating that adequate precision is available from commercially available instruments. Using such instruments, the freezing point measurement can be made in a matter of minutes with a minimum of equipment. The freezing point depression thus appears to be a method which could easily be performed in field laboratories in support of water pollution control tests. However, this author has not yet applied this test under field conditions, nor to a large number of samples and therefore cannot yet attest to its ruggedness and reliability under such conditions.

ACKNOWLEDGEMENTS

Freezing point depression measurements from the Knauer cryoscope were obtained by Huffman Laboratories (Wheat Ridge, Colorado).

RECOMMENDED METHOD FOR TOTAL SOLUTES IN RETORT WATER

Principle

The freezing point of an ideal aqueous solution is lowered 1.86°C for every mole of solute dissolved in one kg of water. The following procedure estimates the total solute content by measuring the freezing point depression.

Comment

Freezing point depression is proportional to the molality of the solution at infinite dilution (One molal = one gram-mole/kg of solvent). However, retort waters containing less than three moles (counting each ion and counter ion separately) are sufficiently dilute to give results accurate to within a few percent. In addition, at such concentrations the difference between

molarity and molality can be neglected for the purpose of this analysis. Results considered as molarity can thus be compared directly with the sum of the individual determinations carried out on the sample.

Applicability

Retort waters containing 0.01 to 3.0 moles/l of dissolved material, counting each ion separately.

Reagents

1. Osmolality* standard. Prepare standards of known osmolality covering the range of concentrations expected in the samples using reagent grade NaCl and de-ionized water. The following table is condensed from more extensive data in Handbook of Chemistry and Physics:

| Wt % NaCl | Total** Molarity (g-moles/l) | Freezing Point Depression (°C) | Osmolality |
|---|---|---|---|
| 0.100 | 0.034 | 0.062 | 0.033 |
| 0.60 | 0.206 | 0.358 | 0.192 |
| 2.90 | 1.01 | 1.729 | 0.930 |
| 6.20 | 2.21 | 3.837 | 2.063 |
| 8.60 | 3.12 | 5.512 | 2.964 |

100 g of each standard is normally sufficient.

* Osmolality is defined as the freezing point depression in °C divided by 1.86°C.

**Total molarity = moles $Na^+$ + moles $Cl^-$.

2. Standard sulfuric acid solution, 1 N (for set-up only). Prepare 1 l of standard 1.00 N $H_2SO_4$ solution from pre-standardized concentrates available from most supply houses. Alternately, $H_2SO_4$ standards can be prepared and standardized according to the directions given in

"Standard Methods" (APHA) or "Methods for the Chemical Analysis of Water and Wastes" (EPA).

3. Aqueous ammonia, 1 M (needed for set-up only). Dilute 67 ml of concentrated (28%) reagent grade ammonium hydroxide to 1 l with d.i. $H_2O$. Standardize by titration with 1 N $H_2SO_4$: To a 100 ml beaker add 25.0 ml of aqueous ammonia and titrate to an inflection point (near pH = 4.6) with $H_2SO_4$ using a pH meter and electrode as indicators. Calculate the ammonia concentration from the expression

$$(NH_3) = \frac{(\text{Volume of } H_2SO_4)(\text{Normality of } H_2SO_4)}{25.0}$$

4. Instrument test solution (needed for initial set-up only). Fill a 1 l volumetric flask 1/2 full with d.i. $H_2O$. Add 100.0 ml of aqueous ammonia. Add 79.06 g of reagent grade $NH_4HCO_3$ and dissolve. Add 29.0 g of acetone and bring to 1 l total volume with d.i. $H_2O$. This solution has a total molarity of 2.6 assuming that the aqueous ammonia is exactly 1.0 M and that complete disassociation occurs:

$$\text{Total molarity} = 1\ M\ NH_4 + 1\ M\ HCO_3 + 0.1\ M\ NH_3 + 0.5\ M\ \text{acetone}$$

Prepare additional instrument test solutions by volumetric dilution with d.i. $H_2O$ to cover the range of interest. Keep all test solutions refrigerated when not in use. Note: The aqueous $NH_3$ must be added before $NH_4HCO_3$ in order to avoid the loss of $CO_2$ from the solution.

Procedure

Most freezing point depression measurements will be made using commercially-available cryoscopes, and the manufacturer's directions should be

followed for this purpose. However, as a minimum the cryoscope should be calibrated with the NaCl standards before and during each series of samples.

It is also recommended that the cryoscope be checked at least once with a series of "instrument test solutions" described above. The measured "NaCl equivalent molarity" should be within 7% of the ideal osmolality if the instrument is to be used for retort waters.

Data Reporting

Plot the measured freezing point depression (or osmolality) vs. the molarity of the NaCl standards. Use this figure to determine the NaCl equivalent total molarity, the total molarity of an NaCl solution giving the same freezing point depression as the sample. Report both the freezing point depression and the NaCl equivalent concentration.

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## SECTION 5

## TOTAL AMMONIACAL NITROGEN IN RETORT WASTEWATERS

Total ammoniacal nitrogen, referred to here as t-$NH_3$, is typically the predominant cationic species in retort water and is frequently of interest to pollution control engineers. The levels of t-$NH_3$ found in retort wastewaters, for example, are believed to inhibit biological oxidation, and such treatment would require the removal and monitoring of t-$NH_3$. The evaluation of other treatment processes, such as reverse osmosis and stream stripping, also requires monitoring of t-$NH_3$. In addition, ammonia in retort wastewaters may be reclaimed and sold to offset the costs of treatment (Probstein and Gold, 1978), thereby providing added incentive for accurate and precise measurements of total ammoniacal nitrogen.

For these reasons t-$NH_3$ has been measured frequently and with a variety of methods. The common methods include (1) direct measurement by ion selective electrode, (2) distillation from a basic medium followed by titration with $H_2SO_4$, and (3) automated or manual colorimetric procedures (Skougstad, 1979; EPA, 1979; APHA, 1976). For example, Wildeman and Hoeffner (1979) and Prien et al. (1977) both determined t-$NH_3$ using method (2). Haas employed method (1) for the analysis of TOSCO II retort water. Fox et al. (1978) compared three methods for the analysis of a wastewater from an in situ process: (1) distillation from a basic solution into $H_3BO_3$ followed by titration with $H_2SO_4$, (2) distillation from a basic solution into $H_3BO_3$ followed by the automated phenolate finish, and (3) direct measurement by ion selective electrode with no distillation. Comparable values for t-$NH_3$ were obtained for all three methods, suggesting that each one would be appropriate for monitoring retort wastewaters.

However, when attempting to apply these procedures in the environment of a field laboratory in support of the simultaneous operation of various pollution control systems, it became apparent that existing tests were unable to provide accurate and reliable results in a timely manner. In such an environment distillation procedures require excessive time, space, and equipment and therefore are not practical. The colorimetric procedures are generally prone to interferences from organic material, alkalinity, and turbidity, all of which are plentiful in retort waters, and therefore were not attempted (APHA, 1976). The ammonia electrodes manufactured by both Orion and Hnu have been applied to various retort wastewaters with unsatisfactory results: the principal difficulty with the electrode technique was the occurrence of erratic shifts in the calibration curve. These shifts were presumably caused by high ionic strength or high organic content of retort waters. Due to these effects, results obtained in the field with the electrode were sometimes inaccurate by a factor of two. Results could be obtained in the laboratory within a precision of ± 20% ($1\sigma$) only by recalibrating after every few samples and repeating the analyses whenever the calibration shifted. Thus, even to obtain results reliable to within 20% required an unacceptable expenditure of labor and excessive time periods. Improved techniques for the measurement of t-$NH_3$ in retort wastewaters were clearly required.

This chapter describes three parallel efforts to develop a practical method for measuring t-$NH_3$ in retort wastewater. Although not anticipated at the onset, three different techniques were developed, each with its own advantages and disadvantages. The first is a modification of the electrode technique which minimizes exposure of the electrode to briny, organic-laden retort waters. The second is an ion chromatographic technique, which also

measures Na and K simultaneously. The third method involves absorption of UV radiation by gaseous $NH_3$ which is evolved from a basic solution.

Early observation of the performance of the ammonia electrode indicated that while the intercept of the calibration curve would change erratically during a series of samples, the slope and intercept would remain relatively constant. The most dramatic changes would often occur when the electrode was exposed to the most concentrated samples; however, such samples could not be anticipated, resulting in frequent recalibration and repetition. The modified electrode technique consists of keeping the electrode immersed in a low level (e.g. 1-10 mg/l) standard adjusted to the ionic strength recommended by the manufacturer. Microliter quantities of the sample are then added to the standard without removing the electrode, and the concentration of the sample is determined by the resulting change in electrode potential rather than by the absolute potential. This procedure will be referred to in this chapter as the sample addition technique (Orion, 1978).

In the ion chromatographic technique the cations in the sample are separated on a low capacity, pellicular, cation exchange resin using a weak acid eluent. The eluent from the cation exchange column proceeds to a column of anion exchange resin in the hydroxide from where the acid eluent is converted to water. The eluent from the second column proceeds to an electrical conductivity detector, where the cations are detected by the resulting change in electrical conductivity. This type of ion exchange chromatography is referred to in the literature as suppressed ion exchange chromatography to indicate the presence of the second column, which suppresses the background conductivity of the eluent (Mulik and Sawicki, 1979). Because of the chromatographic nature of this method, the other monovalent cations in

retort water are also separated, and it is common to observe Na and K during the determination of t-$NH_3$.

It has long been recognized that ammonia vapor exhibits a series of strong absorption peaks in the UV region 180-210 nm (Tannenbaum et al., 1953; Thompson et al., 1963). While those peaks below 195 nm lie in the vacuum ultraviolet, the remaining peaks are easily accessible by instruments available in most laboratories and would seem to be an ideal means for measuring ammonia. Preliminary investigation of the same references indicated that few serious interferences would be found in retort water, assuming that the ammonia in the water sample is evolved into the gas phase by the addition of base. The absorbtivity of ammonia at 197 nm is approximately five orders of magnitude larger than that of either $O_2$ or $H_2O$. The simple amines exhibit broad, relatively unstructured absorption spectra in the same region as ammonia. At the outset of this study it was believed that such amines would not be present in retort waters in sufficient quantities to cause a serious problem.

The possibility of using the absorption spectrum of ammonia as a probe for measuring ammonia in various waters has been investigated by a number of authors. These investigators typically added strong base to an aliquot of sample in a gas bubbler, which was then purged with a continuous gas stream into an absorption cell mounted in an atomic absorption or UV spectrometer. As the ammonia evolved from the basic solution, it was swept into the absorption cell, resulting in a transient absorption peak. Gunther et al. (1956) were one of the first to use this absorption to measure ammonia. Their original observations indicated that the ammonia peaks were sufficiently sharp to require a spectrometer with a band pass of approximately one nm or better in order to achieve a linear calibration curve. They also observed that the

ammonia would gradually decay if left in the light path, a result they attributed to photodissociation. Factors affecting the response of the system to ammonia were studied by several investigators, and these were seen to be the concentration of base added to the sample, the shape and design of the bubbler, the flow rate of the purging gas, and the temperature (Muroski and Syty, 1980; Cresser, 1977; Cresser, 1976; Takahaski et al., 1980). Thus Cresser recommended that the temperature of the sample reaction vessel be controlled to avoid excessive errors. Muroski and Syty also examined this method for interferences due to a number of ions, and observed no effects due to $SO_3^=$, $I^-$, $NO_2^-$, $NO_3^-$, $SCN^-$, $SO_4^=$, $CO_3^=$, $S^=$, and $CN^-$.

In spite of these investigations, the gaseous absorption method has not gained widespread popularity, presumably because of the ease of applying either the electrode method or the automated colorimetric methods to surface and ground waters. However, the results support its application to retort waters, which are analyzed only with difficulty by the standard methods. For this reason the gaseous absorption technique was pursued simultaneously with other approaches.

## EXPERIMENTAL SECTION

Ammonium standards were prepared from analytical reagent $NH_4Cl$ in deionized (d.i.), distilled water. All other chemicals were reagent grade unless mentioned otherwise.

### Sample Addition Technique

Measurements were made with an Orion Research (Cambridge) membrane ammonia electrode, Model 95-10, in conjunction with a Keithley Model 616 Digital electrometer. Potentials were readable to ± 0.1 mV.

Before analyzing samples the electrode was first standardized. After the electrode had been equilibrated as specified by the manufacturer, it was

immersed in 50 ml of 0.1 M NaOH in a magnetically stirred beaker. 10 µl of 10,000 mg/l $NH_4^+$ standard was added to give a solution concentration of 2 mg/l. Successively larger volumes of standard were added to calibrate the electrodes over the range of 2-800 mg/l. These data were then plotted on semi-log paper, producing a straight line at concentrations over 10 mg/l but frequently exhibiting a slight curvature below that level.

Before analyzing the samples, the electrode was rinsed and again immersed in 50 ml of 0.1 M NaOH. 1.0 ml of 250 mg/l $NH_4^+$ was added to give a concentration of 4.90 mg/l, and the cell potential was recorded in two minutes. The sample was added from disposable pipettes, starting with 0.01 ml and proceeding to larger aliquots, until a potential change of 20-30 mV occurred. A reading was recorded after one minute. Additional aliquots of sample were added until a total change of 40-50 mV was recorded.

The concentration in the sample was then calculated based on the change in cell potential. Referring to the calibration figure, it was determined what concentration would have to be present in the beaker to cause the potential change observed. Based on this and the volume of sample injected, the concentration of $NH_4^+$ in the original sample was calculated. This procedure was carried out for the two data points recorded (at 20-30 mV and 40-50 mV), and the results were averaged.

Ion Chromatography

Ion chromatography was performed on a Dionex (Sunnyvale) Model 10 ion chromatograph equipped with a cation separator column (# 030831), cation pre-column (# 030830), and cation suppressor column (# 030834). Eluent was either 5 mM or 7.5 mM $HNO_3$ in distilled water; detection was with the electrical conductivity detector which comes as standard equipment on the Model 10.

Peak signals were processed with a Hewlett Packard Model 3390 digital integrator. Quantitation was by peak height.

Gaseous Absorption Methods--

Original investigations of the gaseous absorption method were carried out with a separate absorption cell and gas evolution chamber, similar in principle to the devices described previously by others. The gas evolution chamber consisted of a 155 ml erlenmeyer flask containing a magnetic stirrer and thermometer. The flask was immersed in a water bath to maintain constant temperature. The absorption cell was a 10 cm heated quartz cell mounted in a Beckman Model DK2-A ratio recording spectrophotometer. The headspace over the sample in the erlenmeyer flask was circulated through the absorption cell and returned to the flask with a variable speed diaphragm pump (Bendix Model BDX44 Super Sampler). In practice, 50 ml of the sample or standard was placed in the flask, 5 ml of 50%, w/w NaOH was added, and the flask was immediately sealed. Stirring was initiated and the headspace gas was recirculated through the absorption cell until a constant value was obtained.

Although this device was used for several preliminary experiments, limitations soon became apparent. The temperature equilibration was too slow, the apparatus needlessly complex, and the measurement cycle too slow. In addition, a somewhat better precision and accuracy was judged to be desirable. For these reasons the majority of work was carried out with the device shown in Figure 5-1, which combined gas evolution, temperature equilibration, and absorption measurement into a single cell. This device was mounted in the sample chamber of a Cary Model 219 UV/visible spectrometer so that the light path passed through the fused silica (Suprasil, Heraeus Amersil) windows shown in the figure (70 mm path length). Rapid temperature equilibration was achieved by circulating water from a temperature bath through the coils

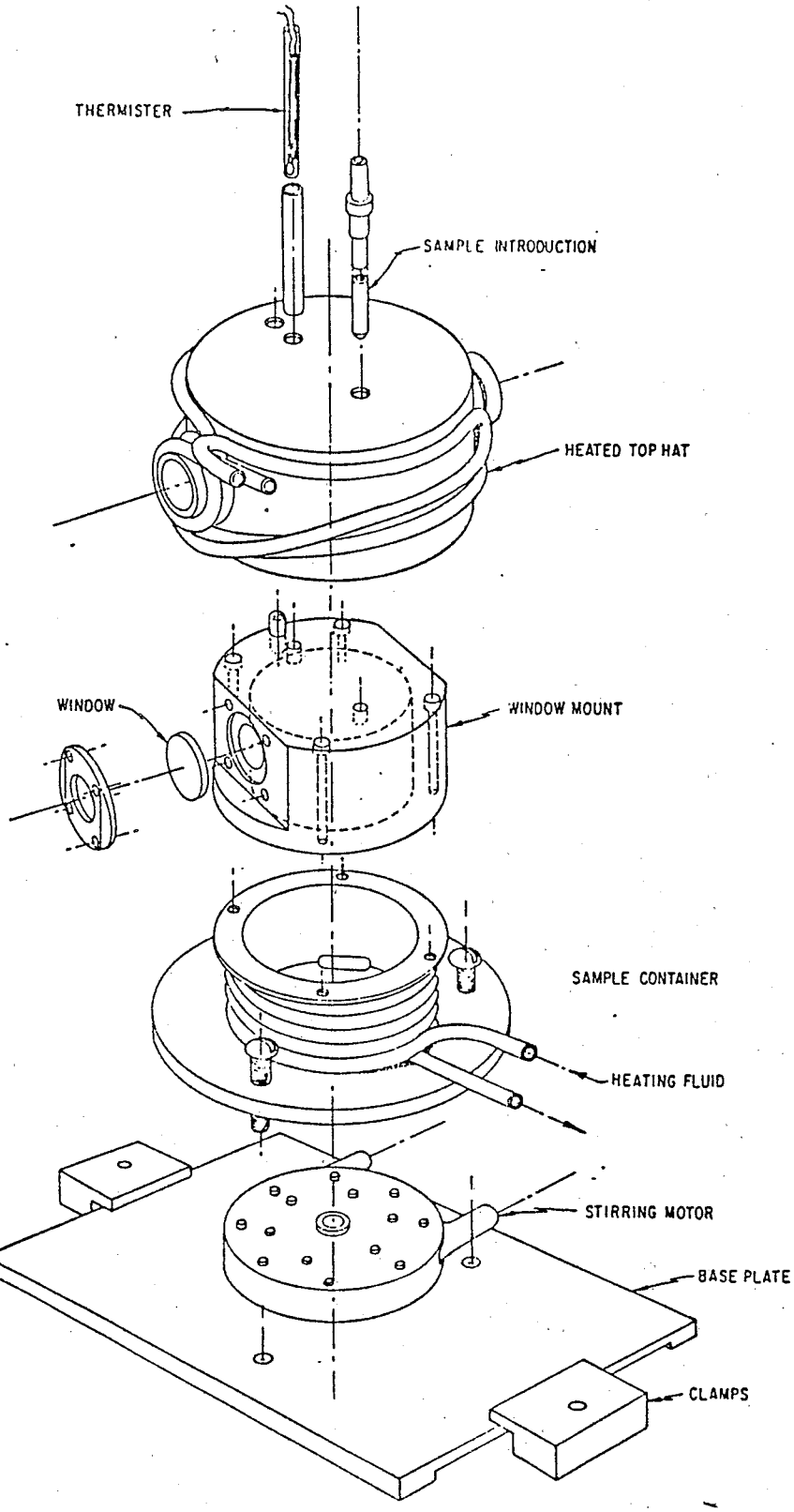


FIGURE 5-1

Sample cell for measuring the uv absorption of gaseous $NH_3$ over a liquid sample

soldered to the chamber body, which was constructed from a stainless steel, 125 ml beaker. Total chamber volume is approximately 150 ml. The top hat in the figure serves to prevent condensation on the windows or window mounting block, a feature which is necessary for work with heated samples. The window mounting block was constructed of acrylic, although it is recommended that future models be made from light metal in order to improve the rate of temperature equilibration of the cell. Stirring of the sample is achieved with the water driven stirring motor shown coupled to a magnetic stirring bar. Temperature of either the solution or headspace is made with the thermister shown. All connections for heating fluid, sample injection, etc. are made with tubing through a demountable wall on the spectrometer, so that the spectrometer sample area need not be opened once the sample chamber is installed.

The sample chamber is mounted in the spectrometer and heating fluid is circulated until temperature equilibration is achieved. Approximately 30 ml of sample or standard is injected followed with 3 ml of 10 M NaOH, both with plastic disposable syringes. After the ammonia has equilibrated between the vapor and aqueous phase, the absorption of the gaseous $NH_3$ at 197 nm is measured, either by scanning across the 197 nm peak or by remaining fixed at the peak maxima. All measurements were made with a fixed bandpass of 0.6 nm with the spectrometer operated in the double beam mode.

## RESULTS AND DISCUSSION

### Sample Addition Method

At the onset of this investigation various approaches were attempted in order to minimize the effect of the drifting intercept of the calibration curve. The first attempt avoided the use of a calibration curve entirely. As with the other procedures, this procedure began by immersing the electrode in a 5 mg/l $NH_4^+$/0.1 M NaOH standard. Aliquots of the sample were then added to

effect potential changes of approximately 20 and 40 mV. Potential and volumes were recorded at each of the three data points, including the 5 mg/l standard. Based on these three data pairs, it is possible in theory to calculate the concentration in the original sample by using the Nernst equation in the form

(1) $$E - E_o = m \log \frac{C}{C_o}$$

$$C = \frac{C_o V_o + V_s C_s}{V_o + V_s}$$

$m$ = slope (constant)

$V_s$ = volume of sample added

$V_o$ = original volume of standard

$C_s$ = concentration in the sample

$C_o$ = concentration of the original standard (i.e., 5 mg/l)

$E_o$ = cell potential for the original standard

$E$ = cell potential after sample addition

and solving for $C_s$. Here the known quantities are $E_o$, $C_o$, $V_o$, and two pairs of $E$ and $V_s$, and the objective is to solve for $m$ and $C_s$. This calculation was carried out by numerical iteration on a Hewlett Packard 9825 desk top computer to a precision of 0.1% relative.

Although computational errors were reduced to negligible amounts, results of this procedure were erratic, the concentration often varying by a factor of two for sequential measurements of the same sample. For this reason the sensitivity of the calculated result to errors in the measured potential was determined by artificially varying the potential which was entered into the calculation. It was observed that 1.0 mV error in a 10 mV potential change caused an error in the calculated concentration of 94% relative; an error of 1.0 mV in a 20 mV change, an error of 30% relative. Since the electrode

potential cannot be measured to better than ± one or two mV due to drifting responses, this approach was abandoned.

The first attempt to incorporate a standard curve into the sample addition technique used the same procedure as described in the Experimental section of this chapter, except that the calibration curve was assumed to be linear (on a semi-log plot). With this assumption the sample concentration is still calculated based on equation 1, except that m is fixed and is obtained from a previously obtained calibration curve. Fixing m results in a greatly simplified calculation which can be carried out with a pocket calculator. However, it soon became apparent that the calibration curve obtained in the laboratory with pure standards exhibited sufficient curvature at concentrations below 10 mg/l to cause a major source of error. This approach was therefore abandoned in favor of the method described in the Experimental section using a plot of the calibration curve to calculate the relative concentrations. However, the approach described above would result in no loss in accuracy should the calibration curve prove linear down to 5 mg/l, as is sometimes the case. The simplified calculation possible with this procedure results in significant time savings to the analyst.

The remaining measurements with the sample addition technique were made using the calibration curve as described in the Experimental section. The precision of this method was estimated by analyzing 12 oil shale retort and synthetic fuel wastewaters in duplicate. Each individual determination itself consisted of the average of two measurements made after two separate sample additions. The average difference between each (averaged) determination was 6% relative. However, this estimate of precision is probably overly optimistic since duplicates were measured sequentially, and perhaps more importantly, the same quantities of sample were added during each analysis. Another estimate of

the precision can be obtained by examining the two concentrations which were averaged to obtain the individual results. Examining 24 such data pairs yields an average difference of 17%, with an average precision of $17/\sqrt{2}$ = 12% for the average of two determinations. Thus, the precision for an individual determination, consisting of the average resulting from two sequential sample additions is 6-12% (1 $\sigma$).

The lower range of the sample addition technique is limited by the necessity of adding sufficient sample to cause a shift in potential which is large enough to measure accurately, while at the same time not adding so much sample that the matrix of the resulting solution is changed. Referring to equation 1 and setting $C_o$ = 5 mg/l, $\Delta E$ = 40 mV, and the maximum value for $V_s$ = 5.0 ml, one calculates a minimum value for the sample concentration, $C_s$ = 210 mg/l. Decreasing $C_o$ or increasing $V_s$ both improve the lower limit, albeit at the cost of poorer performance since the electrode is less stable at lower concentrations and is also affected by changes in the matrix of the sample.

Ion Chromatography

Figure 5-2 is included to illustrate several features of the ion chromatographic determination of ammonia and other ions in retort waters. Figure 5-2a shows the elution of $Na^+$, $NH_4^+$, and $K^+$ using a 7.5 mM $HNO_3$ eluent. $NH_4^+$ and $K^+$ elute close enough to interfere if either are present in large excess. For this reason, among others, quantitation was accomplished with peak height measurements, which are less sensitive than peak area to the occurrence of nearby peaks. Fortunately, $K^+$ is not normally observed in retort wastewaters and the chromatogram shown in Figure 5-2b is typical of those encountered. Both $NH_4^+$ and $K^+N^+$ are clearly resolved and can be quantitated if desired. Figure 5-2c shows a chromatogram for a 10 mg/l standard of $Na^+$, $NH_4^+$, and $K^+$ obtained with a 5 mM $HNO_3$ eluent. The improved resolution between $NH_4^+$

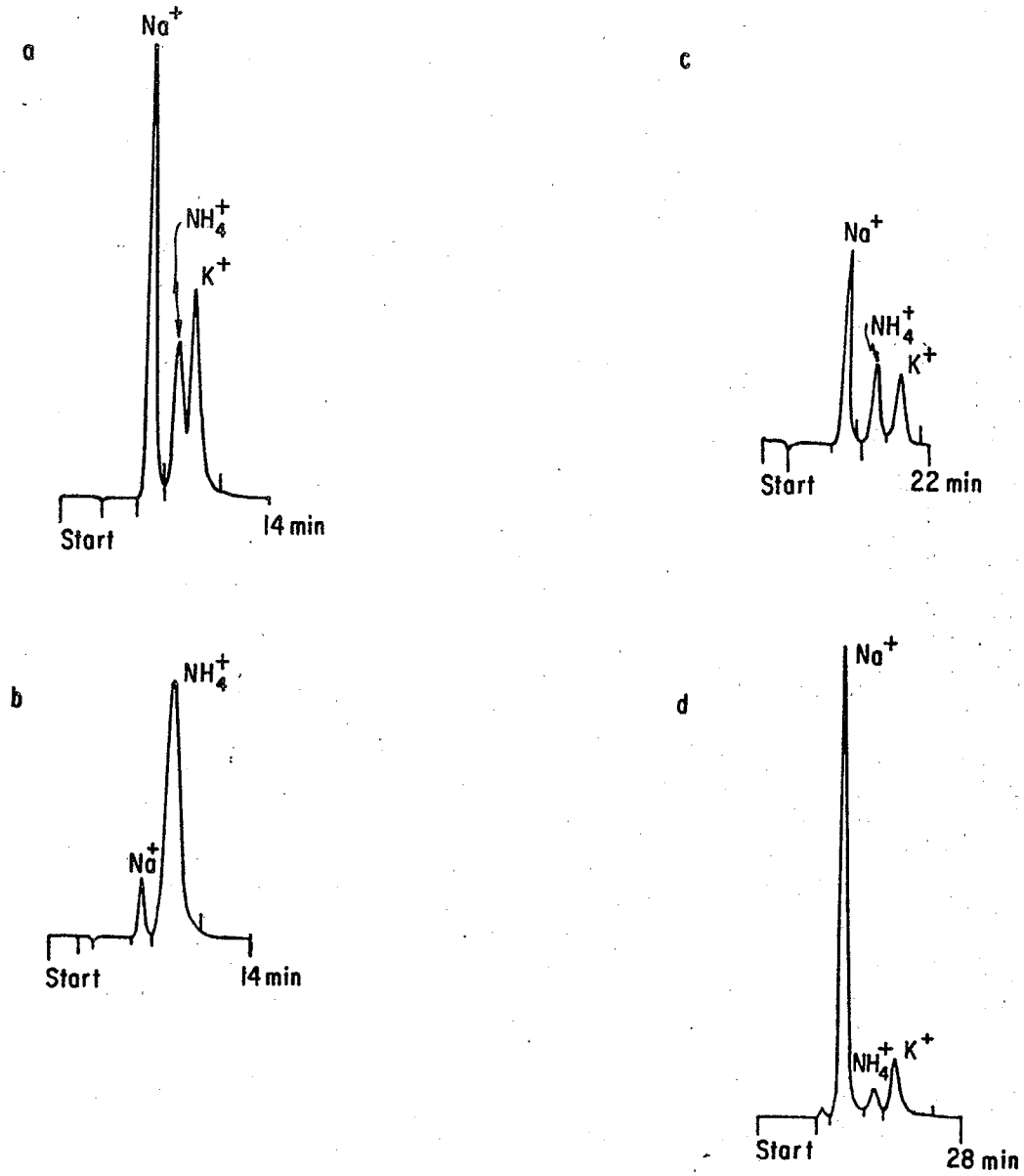


FIGURE 5-2

Ion Chromatograms of $Na^+$, $NH_4^+$ and $K^+$

and $K^+$ resulting from the weaker eluent is readily apparent, and the determination of these three species in the same sample is feasible, assuming the absence of unknown interferences. Methyl amine elutes immediately after the $NH_4^+$ peak, and interferences due to amines should be considered in samples such as retort waters containing high levels of organic material. However, the retort waters analyzed in the authors' laboratory have shown no peak following the $NH_4^+$ peak, suggesting that amines are not a problem in these waters. Figure 5-2d shows a chromatogram of leachate from burned, spent shale. $Na^+$, $K^+$, and a trace of $NH_4^+$ are clearly separated and were reported.

The ion chromatographic method has been used routinely in support of various field tests for a year, and during this time has performed with few problems. However, a gradual deterioration of column performance was noted over this time, especially during the analysis of leachate samples. The latter effect is likely due to the occurrence of large concentrations of alkali earth elements in the leachate which are difficult to remove from the analytical column. Periodic treatment with sodium tartate eluent temporarily improves but does not restore entirely column performance. It is recommended, therefore, that additional precautions be included for such samples. For example, more frequent changing of the pre-column may eliminate degradation of the analytical column due to divalent cations. Most experience with the ion chromatographic system has been with condensates from pilot-scale oil shale retorts and such waters have shown little effect on the column. Column manufacturers now recommend the use of HCl instead of the $HNO_3$ eluent as a means of prolonging column life.

Statistical performance criteria, of course, depend on the exact conditions of the analyses and vary between location, environmental conditions and operator. However, the following has been typical of the authors'

experience. During a two week field test the ion chromatograph was operated in an unheated laboratory where temperatures fluctuated widely. During this period 65 samples were analyzed in duplicate for $NH_4^+$ with an average difference of 2.3%. This difference is somewhat optimistic for such environmental conditions, since sample pairs were analyzed in immediate sequence rather than at different times. For samples analyzed in the laboratory the recovery has averaged 104% (n = 4), not significantly different than unity. The main limitation to reproductibility has been a drifting response, perhaps due to temperature fluctuations, and a slight shift in calibration upon switching suppressor columns, problems which may be minimized in the future by thermally controlling the detector and installing a fiber suppressor column, which can be used continuously. For determination of $Na^+$ and $K^+$ in leachate, the average difference for 6 pairs of samples selected at random was 5.2% and 5.8% respectively. Again, the principle limitation for these species has been a drifting response which occurs as the analytical column is exposed to the high Ca and Mg levels expected in leachate samples.

The dynamic range for $NH_4^+$ is approximately from 1-300 mg/l, although the calibration curve is non-linear throughout parts of this region. Below ~5 mg/l the peak height is proportional to concentration, while above ~10 mg/l peak height is proportional to $\sim(NH_3)^{.5-.6}$. This is reasonable for a weak base which is only partially ionized in the detector.

Gas Absorption Method

Experiments were performed with the first device described in the Experimental Section (separate absorption and gas evolution chambers) to assess in a preliminary manner the feasibility of the gaseous absorption technique. Characteristics of the spectra obtained with standard solutions and real retort wastewaters were initially observed. As expected, artificial standards yielded

spectra with a series of sharp peaks from approximately 210-197 nm (the vacuum uv cutoff for the instrument in use). More importantly, with retort waters a clean ammonia spectrum was observed with no apparent interfering peaks. This observation was especially important because organic compounds absorb in this spectral region, and it was of obvious concern that organic compounds in retort water would evolve and interfere significantly. Closer examination for other absorbing species involved suppression of the ammonia spectrum by acidifying the samples with HCl to a pH of approximately 3. Under these conditions no absorption was observed in the region 210-197 nm, except for one sample which exhibited an intense absorption spectrum consisting of a series of sharp peaks. Based on the appearance of the spectrum (Thompson et al., 1963), as well as the fact that it disappeared when the sample was made basic, this absorption was assigned to $SO_2$. This assignment is also supported by the common occurrence in retort waters of thiosulfate, which decomposes to $SO_2$ upon the addition of acid. Preliminary investigation based on a limited number of samples thus indicated that retort waters when made basic by the addition of NaOH, yielded an easily observed ammonia spectrum free of obvious interfering peaks.

Next, a calibration curve was established using standards over the range 3-300 mg/l, and was observed to be linear over this range but curved at higher concentrations. Using this curve, three retort water samples were analyzed for ammonia. Results compared reasonably with previous analyses by electrode.

Using this same device the importance of temperature control was also established by comparing the absorbance of a 100 mg/l standard over a range of temperatures (Figure 5-3). At 50°C a change of 1°C was seen to cause a 3% change in absorbance, a major source of error, especially since the addition of NaOH to the sample often caused a temperature increase of 5-10°C, which was only slowly dissipated.

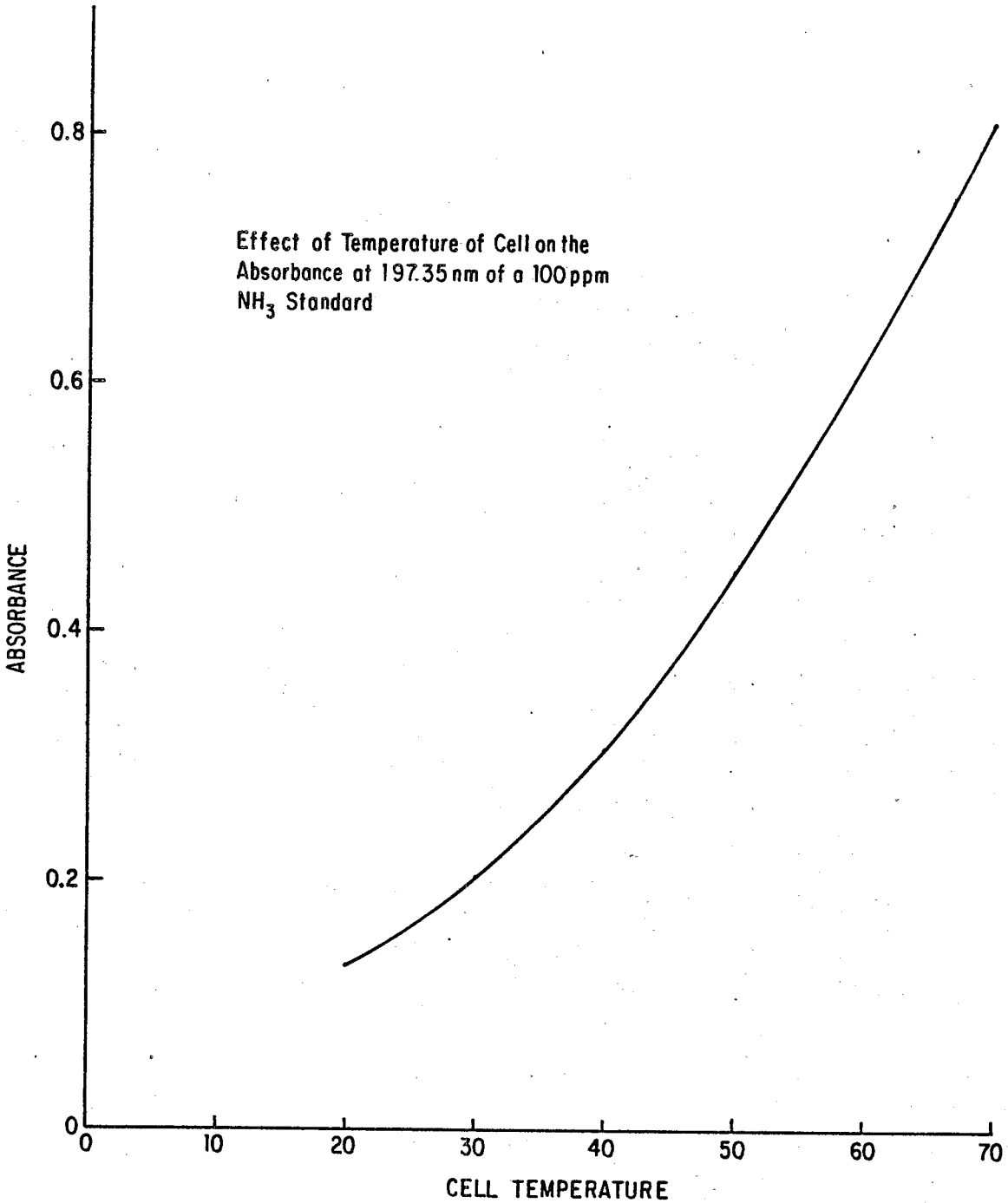


FIGURE 5-3

Effect of cell temperature on response. (Standard concentration = 100 mg/l $NH_3$, absorption wavelength = 197.4 nm)

This implied that better temperature control was required. In addition, a more rapid method of changing samples was required to make this approach practical. For these reasons attempts were made to construct a continuous flow system which would automatically enter the sample, meter the reagents, equilibrate the temperature, and transfer the gaseous headspace sample to the absorption cell. Such a device, modeled after the automated Hg method described in the EPA (1979) handbook was assembled, including a constant temperature bath to maintain temperature control to better than ± 1°C. While this device worked well for standards and even some retort waters, it failed as a general technique for retort waters due to a persistent foaming problem with some retort waters which prevented the complete separation of gas and water phases. This caused liquid sample and reagent to be carried into the absorption cell, resulting in a worthless spectrum and a lengthy cleaning process. Several defoaming agents, such as anti-foam B (Alpkem Corp., Portland), and mechanical separators of various size and design including hydrophobic filters were evaluated, but none proved adequate for all samples. Because the foaming of one sample invalidated the results for all subsequent samples, the continuous flow approach was abandoned in favor of apparatus shown in Figure 5-1.

The cell shown in Figure 5-1 was designed to (1) minimize the effect of foaming, and (2) improve the rate of temperature equilibration. The sample container in this cell is made from 0.025" thick stainless steel as opposed to the standard laboratory glassware used in the original device. The new sample container achieved temperature equilibration for a 30 ml sample in a few minutes.

Tolerance to foamy materials was tested with several samples known to readily produce stable foams, which were introduced into the chamber and

treated normally. Samples for this purpose included 5% Joy dish detergent in water, 5% Joy + 5% vacuum oil in water, 0.07% sodium dodecylsulfate in water, 0.07% sodium dodecylsulfate + 1% 3-in-1 household oil, and several retort waters from a variety of sources. No problems with foaming were encountered with any of these samples, although water could be splashed onto the cell windows if the magnetic stirrer were operated too fast. This cell also overcomes certain disadvantages which have been reported by previous authors for similar flow through devices designed for measuring t-$NH_3$ by gas phase absorption (Muroski and Syty, 1980; Cresser, 1977; Takahaski et al., 1980). While the response of flow-through systems depends on the gas flow rate, no similar phenomenon occurs with the static cell. More importantly, the response is relatively insensitive to the exact volumes of NaOH and sample which are added. Although the samples were introduced only with the precision achievable with a plastic, disposable syringe, the precision of the final analysis was still the the best of the methods tested. (See below.) All results discussed below were thus obtained using this sample cell.

Certain apparent problems should be corrected in future designs. When first placed in the spectrometer, the cell required two hours to stabilize at the desired temperature for analysis. Sample introduced before this period would condense on the windows, where it would remain for hours. This long initial warm up was ascribed to the thermally large window mount, which was made from 16 mm thick acrylic. A window mount constructed from more thermally conductive material would be preferable in the future. In addition, the flat bottomed cell did not drain thoroughly between samples, requiring both water and sample rinses to obtain accurate results. This could be improved by changing the shape of the cell bottom. The stirring mechanism was not sufficiently reliable for routine use and would occasionally stop. Thus, a

mechanically-driven stirrer or a more strongly coupled magnetic stirrer, would appear to be preferable to the design used in this model.

Figure 5-4 shows the spectrum of a 100 mg/l $NH_4^+$ standard over the range 210-188 nm. As can be seen, the peaks become increasingly more sensitive with decreasing wavelength. Although not obvious from the figure, the noise level also increases below 197 nm, making this region less desirable. Possible advantages of using shorter wavelengths were investigated by first flushing the Cary 219 spectrometer with dry nitrogen evolved from a liquid nitrogen tank. However, the lines below 197 nm still tended to be noisier than those of longer wavelength. Background absorption also becomes increasingly important below approximately 200 nm. For example, when deionized, distilled water is introduced into the cell at 60°C, a spectrum is observed in which absorption increases with decreasing wavelength and results in an absorption of 0.004 at 197 nm. Qualitatively, this matches the reported spectrum of water (Thompson et. al., 1963). Since the absorbtivity of water increases approximately ten fold for every 5 nm decrease in wavelength in this spectral region, the use of wavelengths below 197 nm does not appear promising. The remaining experiments discussed in this report were thus performed using the 197 nm peak (spectrometer setting = 197.35 nm) and a band pass of 0.6 nm which represented a compromise between maximum sensitivity and minimum noise.

Three slightly different calibration curves are shown in Figure 5-5 for the concentration range 1-1,000 mg/l. The first curve was obtained with the cell at 50°C using the total height of the 197 nm peak. The second curve was obtained at a cell temperature of 60°C using the same procedure. The third curve was determined by measuring the height of the 197 nm peak above a baseline drawn between the two adjacent valleys to better reject any absorption due to broad-band interfering peaks. The figure illustrates that the calibration

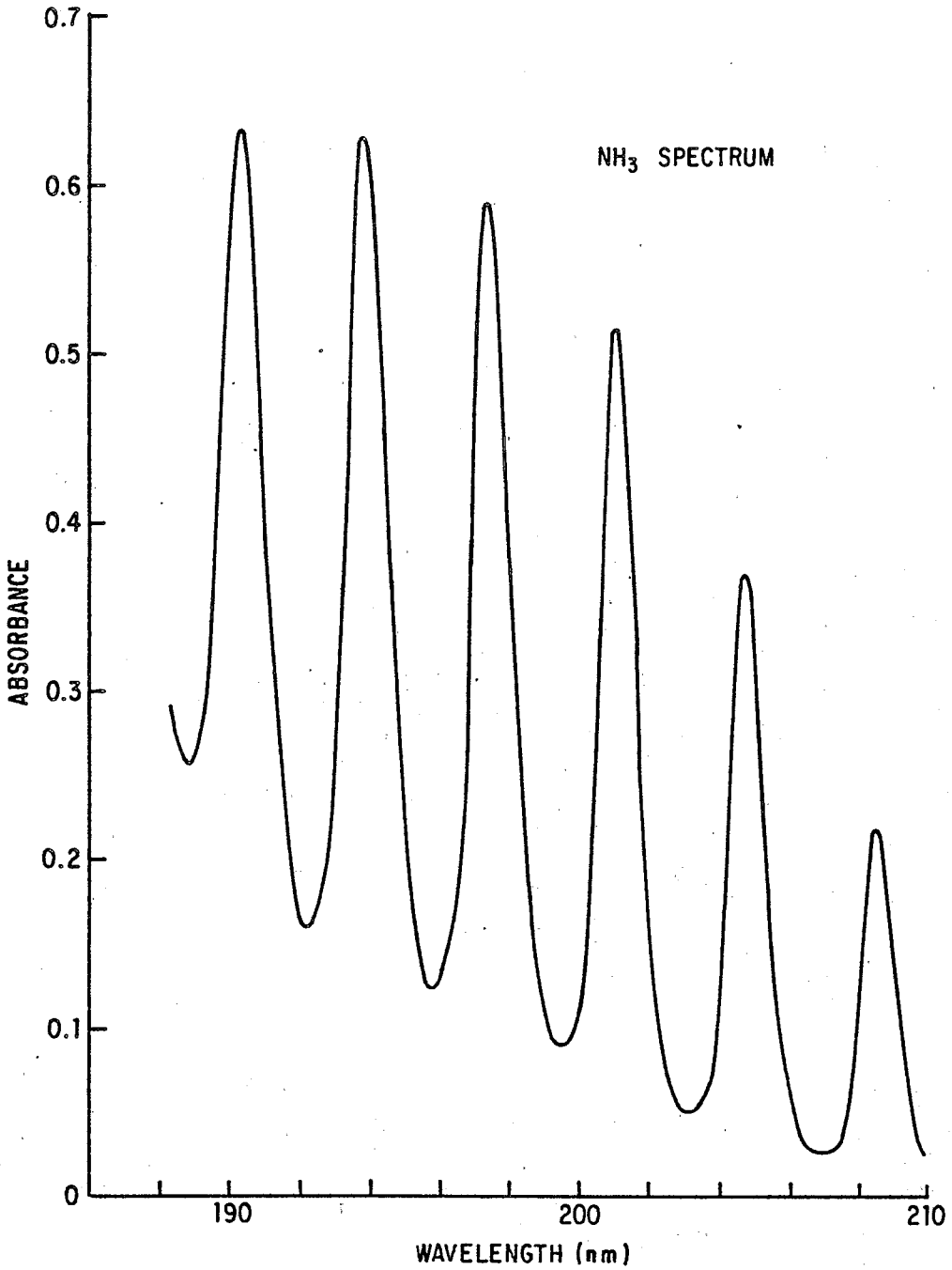


FIGURE 5-4
Spectrum of $NH_3$ in equilibrium with 100 mg/l of $NH_4^+$ at 60°C. (band pass = 0.6 nm)

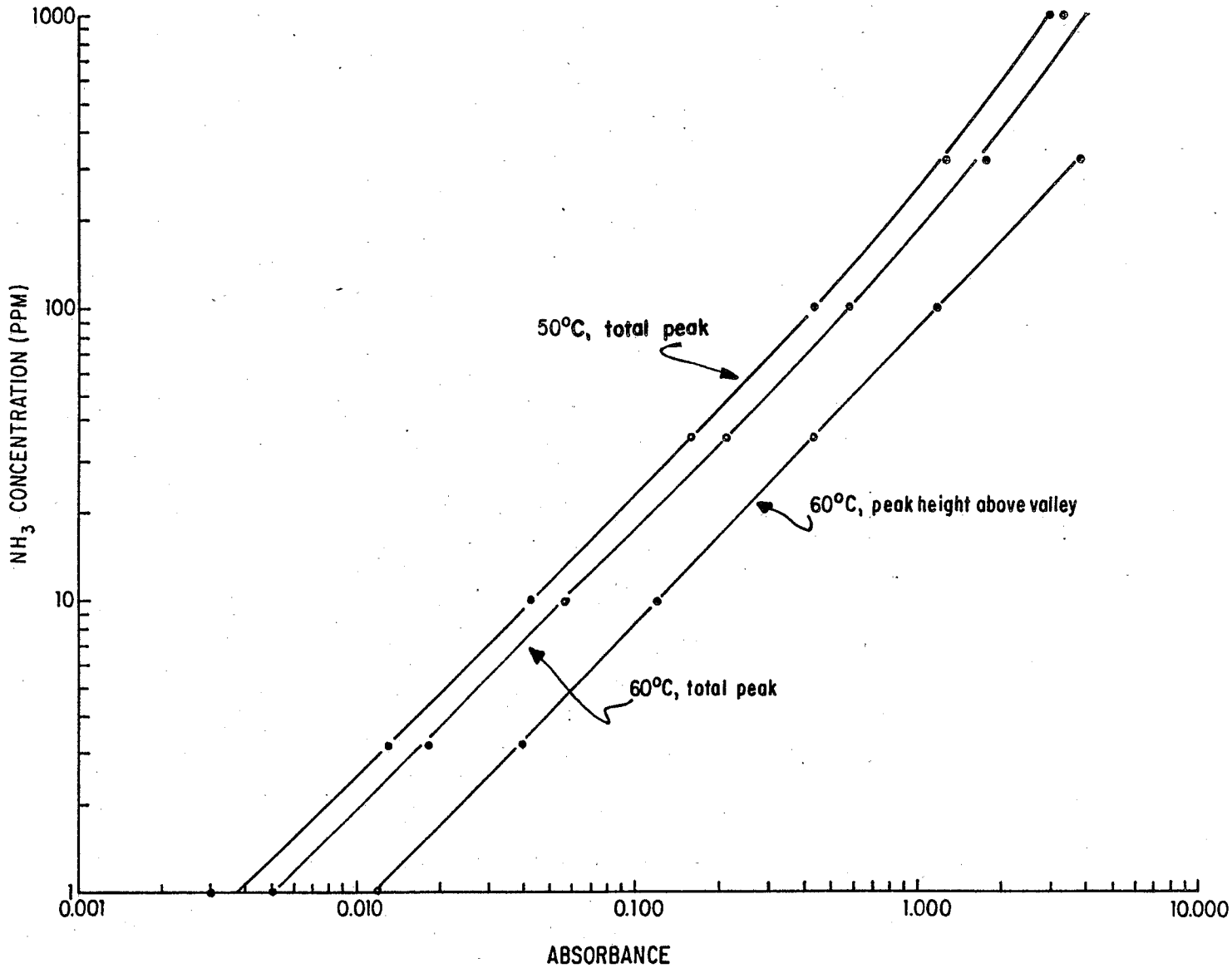


FIGURE 5-5
Calibration curves obtained from the gaseous absorption method

curve is linear from 1-100 mg/l, but slight curvature is apparent at 300 mg/l. Nevertheless, the curve is usable over the entire range except that concentrations above 330 mg/l are not accessible at 60°C. The importance of temperature in this analysis suggests that the range could be adjusted to both lower and higher concentrations by adjusting the temperature appropriately. Considerably higher concentration could also be measured using a cell with a shorter absorption pathlength.

In developing this procedure, the importance of technical procedures become apparent. These included the necessity of choosing a stirring bar of the proper size (ca 15 mm) to provide reliable stirring, and selecting a stirring rate which was fast enough yet did not splash liquid onto the windows. The rinsing procedure between samples could also affect the results, and a rinse with deionized water followed by a rinse with the next sample was found to be necessary for reliable results.

Many retort wastewaters contain a high content of dissolved ions and the gas absorption technique was, therefore, tested for its ability to tolerate samples of high ionic strength. Standards of 33 and 100 mg/l were prepared with and without the addition of strong electrolyte (NaCl at 47 g/l and $Na_2SO_4$ at 8 g/l). When the absorption of these samples was compared, no difference was observed. Thus, the gas absorption technique appears to be insensitive to the occurrence of strong electrolytes at ionic strengths far exceeding that expected in retort waters.

Another major interest in testing the gas absorption method was evaluating its ability to analyze solutions containing high levels of surfactants and oils. The tolerance of the other two methods discussed in this report for surfactants and oils is limited due to fouling of the electrode membrane and to degradation of the chromatograph column. Thus, attempts were made to analyze

solutions containing 100 mg/l of $NH_3$ and the same levels of surfactants and oils used to test the cell with regard to its ability to tolerate foamy samples (see above). These samples contained more oil and surfactant than would normally be expected in a retort water sample and would form a separated layer if allowed to stand for a minute. Success with these samples would therefore imply more than sufficient tolerance to analyze retort water samples. Unfortunately, the analysis of such samples gave rise to certain problems. The equilibration time was excessively long, often requiring 30 minutes. Oils caused a broadband absorption which was 30-50% of the $NH_3$ absorption. (This was subtracted by acidifying the sample to pH 3 and measuring the absorption before adding the base.) The oil often left a residue which required flushing out by pulling room air through the cell until the absorption decreased. Most importantly, when the organic background was subtracted, the absorbance was too low for the concentration of $NH_3$ in the sample. This result was presumably due to the layer of oil which formed over the top of the water in the cell, thereby slowing the transport of $NH_3$ into the gas phase. In the cell used for this experiment the stirring was not sufficient to break the surface of the oil. It is recommended that future designs incorporate a stirring mechanism which is capable of breaking a surface layer of oil.

While the analysis of samples containing large amounts of separable oil must be approached with caution, the results of the gas absorption method with real retort water samples have been much more encouraging. Analyses of retort water samples were performed by two slightly different methods, the first using the total peak absorption at 197 nm, and the second using the height of the 197 nm peak above the two adjacent valleys. (See Figure 5-5). For the first method, the precision based on the six repetitions of the same sample was 0.3%

(one standard deviation). Precision of the second method, identically determined, was 0.6% relative. The recovery for the two methods was 103.6% and 99.3% respectively. The detection limit of the gas absorption method, defined as three times the background noise, was determined by measuring the absorbance of a pure water sample six times. The detection limit so calculated was 0.24 mg/l of $NH_3$. Prudent laboratory practice would thus permit reporting concentrations over approximately 3 mg/l.

Comparison of Methods

In order to establish the veracity of a technique, it is clearly advantageous to compare the results obtained on identical samples using independent techniques. This was done for a set of 12 samples consisting of oil shale retort wastewaters as well as a tar sands wastewater and coal gasification condensate using the methods discussed in this chapter. These results are tabulated in Table 5-1. Waters listed in this table are from various field tests and interlaboratory comparison studies ("round robins"). However the waters are not necessarily representative of the process listed but should cover the spectrum of sample types expected during the treatment of oil shale retort and synfuel wastewaters. Results of the two variations of the gas absorption method are listed, the "single" heading and the "scan" heading referring to the total absorption and peak-above-valley variations discussed previously.

For the purposes of interpretating the data in this table, the ion chromatographic method was used as a reference to which the other results are compared. The average difference listed on the bottom row was then calculated according to the expression

$$\frac{2}{n} \sum_{i=1}^{n} \frac{|x_1 - x_2|_i}{(x_1 + x_2)_i} \qquad (2)$$

Table 5-1

COMPARISON OF AMMONIACAL N MEASUREMENTS OBTAINED BY INDEPENDENT METHODS

| Sample Number | Description | Concentration (mg/l as $NH_3$) | | | |
|---|---|---|---|---|---|
| | | | | Gas Absorption | |
| | | Sample Addition | Ion Chromatography | Single | Scan |
| 1 | Mixed feedwater to steam stripper, 10/6/81 | 895 | 725 | 780 | 720 |
| 2 | Mixed effluent from steam stripper, 10/6/81 | 441 | 370 | 405 | 325 |
| 3 | Geokinetics #17 | 2,128 | 2,200 | 2,300 | 2,150 |
| 4 | Dilute Paraho | 6,736 | 6,000 | 6,400 | 6,250 |
| 5 | Oxy-6 | 8,197 | 8,500 | 8,600 | 8,400 |
| 6 | S-7, reflux from steam stripper | 11,290 | 10,200 | 11,000 | 9,800 |
| 7 | Concentrate from reverse osmosis treatment | 4,702 | 3,700 | 4,400 | 4,200 |
| 8 | S-11, reflux from steam stripper | 12,934 | 12,000 | 14,800 | 12,000 |
| 9 | S-3, reflux from steam stripper | 18,282 | 17,500 | 19,800 | 17,000 |
| 10 | Omega-9 (3,125) | 3,595 | 3,300 | 3,600 | 3,450 |
| 11 | Tar sands wastewater | 73 | 55 | 102 | 50 |
| 12 | Condensate from coal gasification | 3,903 | 4,000 | 4,200 | 4,200 |
| Average difference | | 12% | 0.0% | 13% | 5% |

The average difference for the sample addition method is reasonable considering the precision of the two methods involved in the calculation. Furthermore, no systematic bias is apparent, and the accuracy of the standard addition method is therefore limited by its precision. Similar statements can be made for the scanning variation of the gas absorption method, except that agreement of this method to the ion chromatographic method is better. The five percent agreement between these two methods suggests that both are accurate to that amount or better. However, the single wavelength variation of the gas absorption method clearly gives results which are biased high, since every result obtained with this method is higher than the corresponding result obtained with the scanning variation and ion chromatographic method. This bias is most evident for sample 12 (tar sands wastewater), but is less pronounced for the other samples. In spite of the obvious bias with the single wavelength variation, the results obtained with this method agree on the average with the ion chromatographic results as well as do the results from the sample addition method. This reflects the better precision of the absorption technique.

In completing the analyses using the single wavelength variation, attempts were made to correct for background absorption by first neutralizing or acidifying the sample and measuring the resulting absorption. The sample was then made alkaline and the resulting absorption measured. Using this procedure, corrections for background absorption were negligible. Apparently, the background absorption resulting in the high bias for the single wavelength variation results from compounds which are volatile in alkaline but not in neutral or acidic solution. Thus, while the identity of the interfering material in this technique has not been established, it must be an organic base. Organic amines are possibilities although their presence has not been

reported in oil shale retort wastewaters in significant quantities. Examination of spectra obtained with selected samples confirms the presence of broadband absorbing species. Thus, the background spectrum can be calculated by measuring the peak height above the valley and calculating the background by comparison to the spectrum of pure $NH_3$. The results of such a calculation are shown in Figure 5-6. While the background is clearly a significant part of the total absorption, not enough detail is present to suggest a particular compound or class of compounds.

Performing the methods described in this chapter confirms that each has definite advantages and disadvantages. The sample addition method requires the minimum investment in equipment, the major items being an electrometer, an ammonia electrode, and a set of microliter pipettes. It is also highly labor intensive and automation of this procedure would require a substantial effort. The ion chromatographic method can be performed with commercially available equipment, the principal items being a suppressed ion chromatograph and peak integrator or strip chart recorder. Labor requirements are less than the other methods and consist primarily of periodically checking on the proper operation of the instrument and reducing the data. The major difficulty with the ion chromatograph has been degradation of the columns when exposed to Ca and Mg and the drifting response which occurs over time or when the suppressor columns are exchanged for regeneration. The gas absorption method with background correction appears promising as a continuous, on-line monitor because of the simplicity of the measurement and the minimum sample handling requirements. Optical absorption instruments are often used for process monitors because of their inherent simplicity and ruggedness, yet no suitable gas absorption instrument is presently available. If such an instrument is developed, it should include a method for correcting broadband background absorption. This

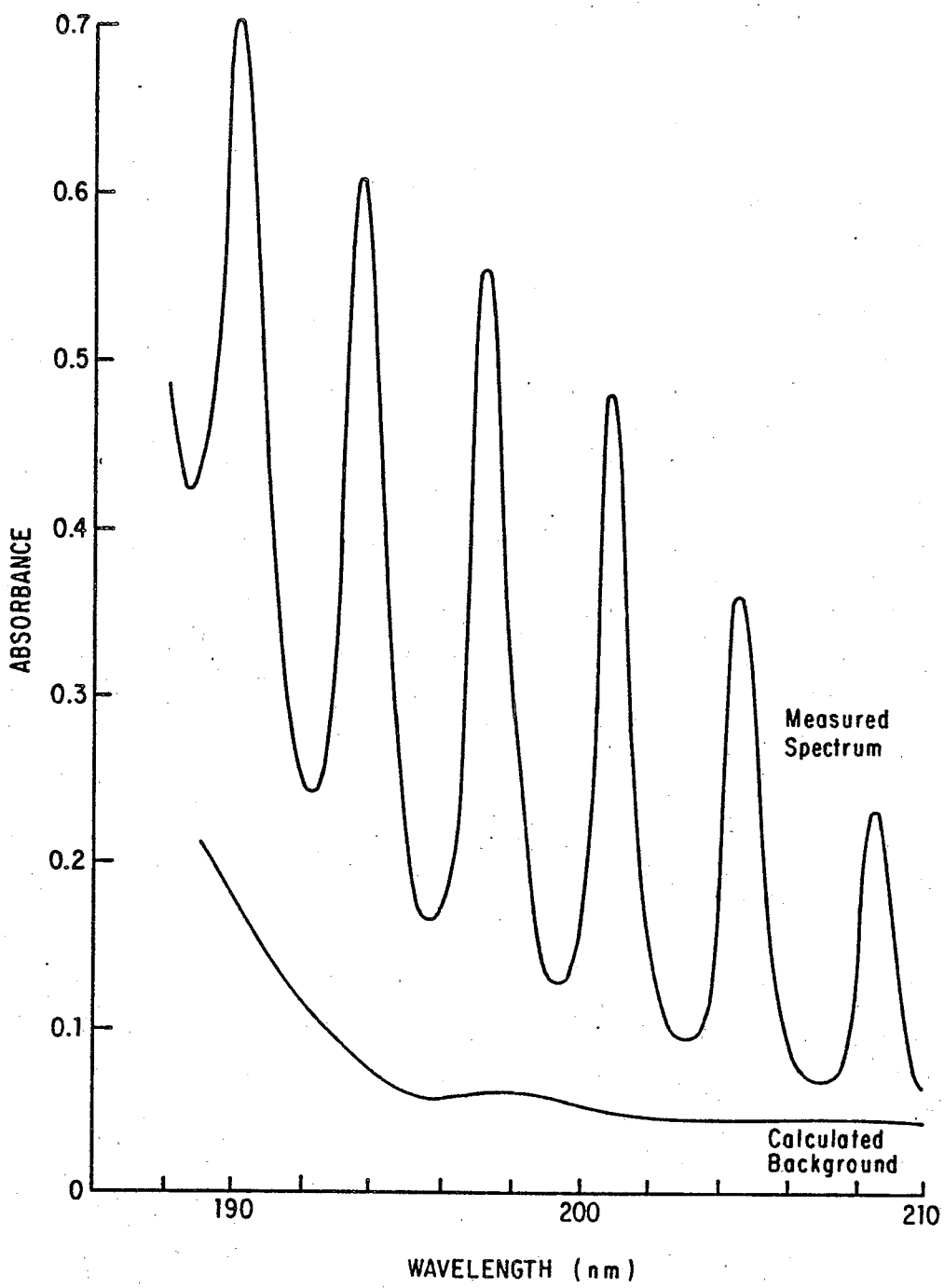


FIGURE 5-6

Gas absorption spectrum over a retort wastewater

could complicate the device somewhat. Another advantage of the gas absorption method is that it responds only to ammoniacal N in the form of aqueous $NH_3$. This device could thus be used to distinguish between aqueous $NH_3$ and $NH_4^+$ and also to measure the volatility of ammoniacal N as a function of temperature and pH, a measurement of interest to those involved in removing ammoniacal N from wastewaters.

PROTOCOL FOR TOTAL AMMONIACAL N BY ION CHROMATOGRAPHY

Principle

$NH_4^+$ is separated from the concomitant cations on a cation exchange resin using weak acid eluent. The $NH_4^+$ is detected by electrical conductivity after the conductivity of the eluent is suppressed by passage through an anion exchange resin in the $OH^-$ form.

Comments

This method also measures Na and K simultaneously with $NH_4^+$. However, K co-elutes with methyl amine and therefore cannot be quantitated when both are present.

Samples with major amounts of alkaline earth metals cause the separator column to degrade. Such samples (e.g., leachates) must therefore be approached cautiously.

The experimental work supporting this method was performed on a suppressed ion chromatograph. No comment is made or implied regarding the efficacy of non-suppressed ion chromatographs.

Reagents and Supplies

1. Ammonia-free water. Waters stored in the laboratory are frequently contaminated due to the ubiquitous presence of $NH_3$. It is therefore important to check the purity of the water used to make up reagent solutions by injecting an aliquot into the ion chromatograph. No $NH_4^+$ peak should be visible on the recording.

2. Ammonia stock solution 10,000 mg/l as $NH_3$. Dissolve 31.30 g of analytical reagent grade $NH_4Cl$ in water and bring to 1.00 liter volume with ammonia free water.

3. Stock Na solution, 10,000 mg/l as Na. Dissolve 25.42 g of analytical reagent grade NaCl and bring to 1.00 liter volume with ammonia free water.

4. Stock K solution, 10,000 mg/l as K. Dissolve 19.07 g of analytical reagent grade KCl and bring to 1.00 liter total volume.

5. Mixed working standards. Prepare mixed standards over the range of 1-330 mg/l. Because the calibration relationship is often curved, especially near the end of the working curve, the standard concentrations should bracket the sample concentration.

6. Disposable syringe, 3 or 10 ml capacity. Exposure of the samples and standards to the atmosphere can be minimized by outfitting the syringe with barbed adaptors to permit the connection of small tubing. Transfer of the sample or standard into the syringe can then be effected conveniently with minimum exposure to air.

7. Syringe-type filters, 0.45 μm pore diameter. The samples should be filtered before injection into the chromatograph. This is accomplished most easily with a filter holder which fits into the luer-lock syringe tip during injection of the sample.

8. Eluents. Prepare a stock solution of 1 M HCl or $HNO_3$ using concentrated, pre-standardized reagent available from most supply houses.

   a. 7.5 mM eluent is used for $Na^+$ and $NH_4^+$ but does not adequately separate $K^+$. Add 30 ml of the stock solution to a 4 liter container and bring to volume.

   b. 5.0 mM eluent is used to separate $Na^+$, $NH_4^+$ and $K^+$. Add 20 ml of stock solution to a 4 liter container and bring to volume.

Apparatus

1. Suppressed ion chromatograph equipped with a 100 µl sample loop, electrical conductivity detector, and a standard cation separator column and pre-column.
2. Dual channel strip chart recorder with separate ranges or a digital peak integrator capable of reporting peak height.
3. Apparatus or supplies for diluting samples up to 1,000 fold.

Procedure

Refer to the operator's manual of the ion chromatograph for general operating procedures.

The operating range of the instrument equipped with a 100 µl injection loop is approximately 1-300 mg/l. However, this can be readily shifted to a higher range by decreasing the volume of the sample loop, should the operator wish to avoid diluting samples and has no need for the lower concentration measurements.

While the analysis can be performed with a single suppressor column, it is recommended for routine work to include two suppressor columns. The second suppressor column can be regenerated while the first column is in use, so that a suppressor column is always available. Otherwise, all analyses must stop while the suppressor column is regenerated. An alternative to the use of two suppressor columns may be the use of a single cation fiber suppressor which needs no regeneration. This device has recently been made commercially available but has not yet been tested in the authors' laboratory.

To begin the analysis, inject a series of standards covering the range 1-300 mg/l. Plot the resulting peak heights on log-log paper and select a region on the calibration curve which is linear or nearly so. Because the response of the ion chromatograph often drifts during the course of analyses,

it is important to recalibrate periodically, including before and after each series of samples and upon changing suppressor columns. It is frequently more convenient to maintain the calibration of only part of the possible dynamic range, and to dilute samples to fall within that range.

Samples are injected identically to the standards and are quantitated by use of the calibration curve prepared as described in the last paragraph.

The precision of this analysis should be determined, not by repeating a series of samples in sequence, but by operating a set of samples spaced over a several day period. The latter approach will include contributions due to instrument drift, while the former approach may result in an overly optimistic estimate.

PROTOCOL FOR TOTAL AMMONIACAL N BY MODIFIED ELECTRODE METHOD

Principle

An ammonia ion selective electrode is maintained in a solution of pure $NH_4Cl$ standard to which small amounts of sample are added. The concentration in the sample is determined by the change in potential upon addition of the sample.

Comments

This method is applicable to samples containing 200 mg/l or more of ammoniacal N. It requires less equipment than the ion chromatograph method but is also more labor intensive and less precise.

Reagents and Supplies

1. 0.1 M NaOH. Add 4.0 g NaOH to a 1 liter flask. Dissolve and bring to volume with deionized water. Prepare 50 ml per sample. Note: water contaminated with $NH_3$ will make this analysis more difficult by causing increased curvature of the working curve. See APHA (1976)

method 418A for methods to minimize $NH_3$ contamination of reagent water.

2. $NH_3$ stock solution, 10,000 mg/l of $NH_3$. Dissolve 31.30 g of analytical reagent grade $NH_4Cl$ in d.i. water and bring to 1 liter total volume.
3. Working $NH_3$ standard, 1,000 mg/l. Dilute 10.0 ml of the 10,000 mg/l stock solution to 100.0 ml total volume.

Apparatus

1. Ammonia ion selective electrode, membrane type.
2. Electrometer, suitable for use with ammonia electrode and readable to ± 0.1 mV on 100 mV scale.
3. Beakers, 100 ml, one per sample.
4. Magnetic stirrer.
5. Set of micropipets covering the range 10-1,000 µl. A set including volumes of 10, 25, 50, 100, 250, and 1,000 µl is suitable.

Procedure

1. Preliminary. Place 50.0 ml of 0.1 M NaOH in a 100 ml beaker, add a magnetic stirring bar, and immerse the electrode at a slight angle to discourage the formation of bubbles on the surface. Begin stirring and observe the potential. This potential should be at least 60 mV less than the potential of the 2 mg/l standard prepared below. A smaller difference suggests contamination of the 0.1 M NaOH with $NH_3$.
2. Standardization. To the beaker prepared in the previous step, add a series of aliquots of $NH_3$ standard stock solution to prepare a series of standards. Record the cell potential after each addition, allowing

a few minutes for the electrode to stabilize. A suitable series of standards follows:

| Aliquot Volume (µl) | Concentration of Solution Added (mg/l) | Total Volume (ml) | Final Concentration in Beaker (mg/l) |
|---|---|---|---|
| 100 | 1,000 | 50.10 | 2.00 |
| 250 | 1,000 | 50.35 | 6.95 |
| 50 | 10,000 | 50.40 | 16.9 |
| 100 | 10,000 | 50.50 | 36.6 |
| 250 | 10,000 | 50.75 | 85.7 |
| 1,000 | 10,000 | 51.75 | 277 |
| 3,000 | 10,000 | 53.75 | 825 |

Plot the log of the concentration vs. the cell potential on semi-log paper. Repeat this calibration procedure to assure that the slope and shape of the curve is reproducible. Remove and rinse the electrode.

3. Analysis. Add 50.0 ml of 0.1 M NaOH to a 100 ml beaker as above. Immerse the electrode and begin stirring. Add 0.250 ml of 1,000 mg/l standard, resulting in a concentration of 4.98 mg/l, and record the cell potential, $E_0$, after allowing a few minutes for equilibration. Begin adding the sample, starting with 10 µl aliquots and progressing to larger volumes until a total change in cell potential of approximately 20 mV occurs. Record the cell potential, $E_1$ and total volume added to this point. Proceed to add larger volumes, up to 5.0 ml, until a total change of approximately 40 mV is observed. Record the cell potential, $E_2$, and the total volume added to this point.

4. Calculation. The sample concentration is calculated based on the potential difference $E_1$-$E_0$ and $E_2$-$E_0$ and not on the absolute cell potential. Consider first $E_1$. Referring to the calibration plot

prepared in Step 2, set $E_o$ to the potential corresponding to 4.98 mg/l. Determine the concentration resulting in a potential increase of $E_1$-$E_o$ and call this C. The sample concentration calculated at this point is then given by:

$$C_s = \frac{C\ (V_1 + 50) - 250}{V_1}$$

Where volumes are in ml and concentrations in mg/l. Repeat this calculation for the second data point ($E_2$, $V_2$) to obtain a second estimate of $C_s$. Average these two results.

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## SECTION 6

## TOTAL SULFUR IN RETORT GAS

In addition to liquid fuel, oil shale retorting produces a synthetic fuel gas, known as retort gas, as a major energy-containing product. The composition and volume of retort gas vary widely depending on the retorting process, and analytical methods developed for such gas must be insensitive to matrix composition. For example, retorting processes which heat the oil shale with a heat exchange media ("indirect processes") produce a gas containing approximately 80-100% combustible components ($H_2$, CO and hydrocarbons) with a heat content of approximately 1,000 Btu/SCF (~9 kcal/l). The direct retorting processes, which combust a portion of the oil shale in the retort, yield a gas containing approximately 80-90% inert material ($N_2$, $CO_2$) with a heat content approximately ten times less (Nevens et al., 1980).

A major air pollution concern associated with proposed oil shale development is the emission of S contained in the retort gas. Untreated retort gas may contain S gases at percent levels in the form of COS, $H_2S$, $CS_2$, or various mercaptans. However, since present development plans call for the combustion of retort gas as a source of steam and electricity, the various S compounds would be emitted as $SO_2$.

Numerous S-control technologies, such as the Stretford process and various amine scrubbing techniques, are presently being considered for the removal of S species from retort gas prior to combustion, and such systems may be field tested during the coming years. It is thus important that a means be available for measuring total S in retort gas so that the control efficiency of such devices can be determined.

A measure of total S is also needed for quality control purposes as a check on the determination of the individual S species. As discussed in Chapter 7, methods are not available at the present time for the determination of all possible S species in retort gas. Even if such methods were available, the difficulty of calibrating for each species would normally be too time consuming to perform routinely. A measurement of total S thus provides some assurance that major species have not been overlooked or measured incorrectly.

The method should be sufficiently rugged for use in a field laboratory. In addition, automatic and rapid operation is essential. Reagent requirements should be minimal. The analytical technique must also be compatible with a sampling system which avoids cooling the sample or otherwise exposing the sample to liquid water, since the S species found in retort gas may be removed by exposure to condensed water (Wallace, 1980).

Of the instruments available for measuring total S in related types of samples, the flame photometric detector (FPD) is probably the most common (APHA, 1977). However, several characteristics of this device suggest that it is particularly unsuited for retort gas. These characteristics include interferences due to hydrocarbons and perhaps $H_2$ and $CO_2$, instability of the flame upon exposure to combustible gases, and a dynamic range which is too low ($\sim 10^{-10}$ - $10^{-7}$ g/sec) for retort gas. The latter feature requires that retort gases be diluted approximately 1,000 fold prior to introduction into the flame, an operation which is difficult to perform well even under laboratory conditions. In addition, the response of the FPD is compound-specific, that is, the response per mass of S depends on the type of S compound (Wallace, 1980; Lucero and Paljug, 1974; Gangwal et al., 1979; Pearson and Hines, 1977; Doehler et al., 1977). The latter feature would be particularly

troublesome when trying to determine S in retort gas without a prior knowledge of the forms of S present.

ASTM method D 1072 provides a manual method for measuring total S in a combustible gas. In this method the fuel gas is burned, the combusted S gases are scrubbed in a solution of $Na_2CO_3$, oxidized to $H_2SO_4$, and titrated with $BaCl_2$. This method is obviously time consuming, although the basic chemistry appears sound.

A second ASTM method, D 3031, provides for the determination of trace levels of S in natural gas by hydrogenating the sample in a hydrogen stream at 900°C and determining the $H_2S$ produced with the methylene blue method. This method also appears time consuming, and it is questionable whether the hydrogenation step would work as efficiently with retort gas as with natural gas.

Aside from the FPD, the literature in general describes two main categories of instruments for measuring S in hydrocarbon matrices: those which reduce all S compounds to $H_2S$ prior to analysis, and those which oxidize all S compounds to $SO_2$ or $SO_3$. Both methods are discussed extensively in the literature (Kolthoff and Elving, 1961; Kuck, 1978; Wallace, 1980). In summary, either operation can be performed quantitatively, although problems with coking have been reported in reductive systems. For this study an oxidative approach was selected because of the ready availability of continuous and interference-free $SO_2$ analyzers. The objective was then to develop a system for producing $SO_2$ in constant proportion for each of the various S compounds.

This goal was first attempted by passing various S compounds through a heated tube in the presence of air, an approach which is used in several laboratory instruments (Martin and Grant, 1965; Wallace et al., 1970; Culmo, 1972). When this approach failed, the next approach was to pass the S gases

through a flame, an approach which achieved stoichiometric conversion of all the S compounds tested.

The final system was challenged with a variety of S compounds to test its ability to measure total S independently of molecular form. Finally, the integrated sampling and analysis system was field tested during operation of the 150-ton simulated in situ retort located at the Laramie Energy Technology Center. The data presented in this paper suggest that the system developed should be applicable to a wide variety of synthetic fuel gases as well as oil shale retort gas.

EXPERIMENTAL

Gas flow rates were measured with Matheson Model 7642T rotameters calibrated with the gas in use. Selected flow measurements were also made with a Tylan mass flow meter with sensing heads covering the range 1-1,500 sccm. The calibration of gas flow equipment was carried out with either dry test meters or bubble meters, both of which were calibrated in reference to NBS standards. Liquid flows were controlled with a Fisher Labortechnik syringe pump which had been calibrated gravimetrically.

Gas standards of the volatile gases--$SO_2$, $H_2S$, and COS--were prepared by dilution with a flowing stream of carrier gas--either $H_2$ or $N_2$. Gas standards for the less volatile species, $CS_2$, dimethyl disulfide and thiophene, were prepared by metering a constant flow of liquid into a flow of diluent. Evaporation occurred in a glass tube under a heat lamp. Gas standards of methyl mercaptan were prepared by metering a flow of 0.40% methyl mercaptan in $N_2$ into a flowing diluent stream.

$SO_2$ was detected with a Thermo Electron Corp. Model 40, pulsed fluorescence stack gas monitor. The range of this device is approximately 5-5,000 ppmv. All gases were supplied by Matheson. Reagents were as follows:

Thiophene, analytical reagent grade (Mallinckrodt); 0.4% methyl mercaptan in $N_2$, analyzed mixture (Matheson); Thiophene liquid (Eastman); Methyl mercaptan liquid (Eastman); $CS_2$, analytical reagent (Mallinckrodt).

RESULTS AND DISCUSSIONS

A large number of S species can conceivably occur in retort gas and it was not feasible to test the conversion of every possible gas. Therefore, a group of six compounds representative of different compound classes were selected for detailed testing. These included $SO_2$, $H_2S$, COS, methyl mercaptan, thiophene, and carbon disulfide.

Measurement of total S requires that all forms of S in the retort gas must be converted to a species which can be readily measured. Because of the ready availability of reliable and accurate $SO_2$ monitors, attempts were made to develop a method which would convert all S compounds to $SO_2$ with the same conversion efficiency. This was first attempted by passing the gases of interest through a heated tube in the presence of air. The heated tube used in these experiments was approximately 12" long by 1" diameter and packed with Raschig rings. A residence time of approximately 4 seconds was required to effect optimal conversion. Effluent $SO_2$ was measured by a pulsed fluorescence $SO_2$ monitor which had been calibrated with pure $SO_2$. Results were compared to values expected for 100% conversion.

Two main problems were evident with this approach. When $SO_2$ was introduced into the heated tube, 100% recovery was achieved with temperatures up to 720°C. Above this temperature loss of $SO_2$ occurred, presumably due to formation of $SO_3$. When introducing $H_2S$ into the heated tube, a temperature of at least 650°C was required to effect 100% conversion. Unfortunately, in the temperature range 650-720°C the conversion of carbon disulfide, methyl mercaptan, and thiophene were incomplete and variable, approximately 84, 83 and

93%, respectively. Thus, the problems with this approach were (1) the dependence of the conversion efficiency on temperature and molecular form, and (2) the production of significant amounts of $SO_3$ which would be expected to damage eventually the optics of the $SO_2$ monitor.

These results can be explained by consideration of Figure 6-1, which shows that the equilibrium for the reaction $SO_2 + \frac{1}{2}O_2 = SO_3$ is highly dependent on both temperature and oxygen content at temperatures below 1,500°C. Significant amounts of $SO_3$ can be formed in this range. Dependence upon oxygen content is also an important consideration since retort gases contain variable amounts of fuel which would consume variable amounts of the added combustion air.

One approach to this problem would be to find a catalyst which would selectively convert all species to $SO_2$ even when operated well below 1,500°C. However, a more straight forward approach, and the one used in this effort, is to carry out the conversion at temperatures well above 1,500°C where 100% conversion is most likely. In order to achieve a sufficiently high temperature, a flame was used as a converter in all subsequent experiments.

Laboratory experiments were conducted to determine the conversion efficiency of a methane/air flame using the apparatus illustrated in Figure 6-2. Artificial standards were introduced through the inlet labeled "sample," and the response of the $SO_2$ monitor was compared for the various species. The $SO_2$ monitor was calibrated with a known concentration of $SO_2$ introduced without passage through the flame, so that the absolute as well as the relative conversion efficiencies could be determined. The condenser shown was included because the combustion gases from the flame contained more water than could be tolerated by the $SO_2$ monitor.

The device shown in Figure 6-2 was entirely enclosed to avoid contamination of the combustion gases by air prior to analysis. This was achieved by

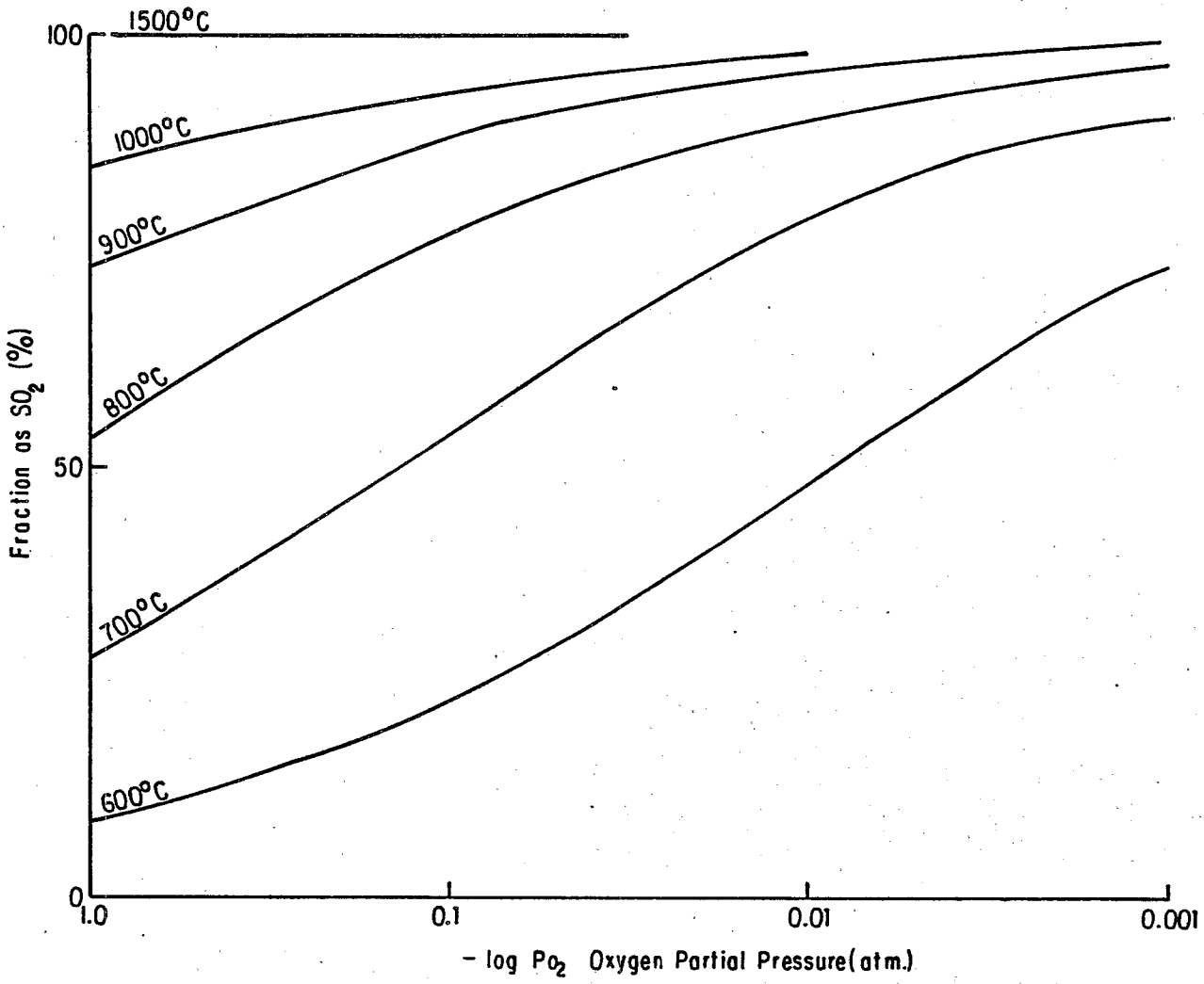


FIGURE 6-1

Equilibrium for the reaction $SO_2 + 1/2O_2 = SO_3$

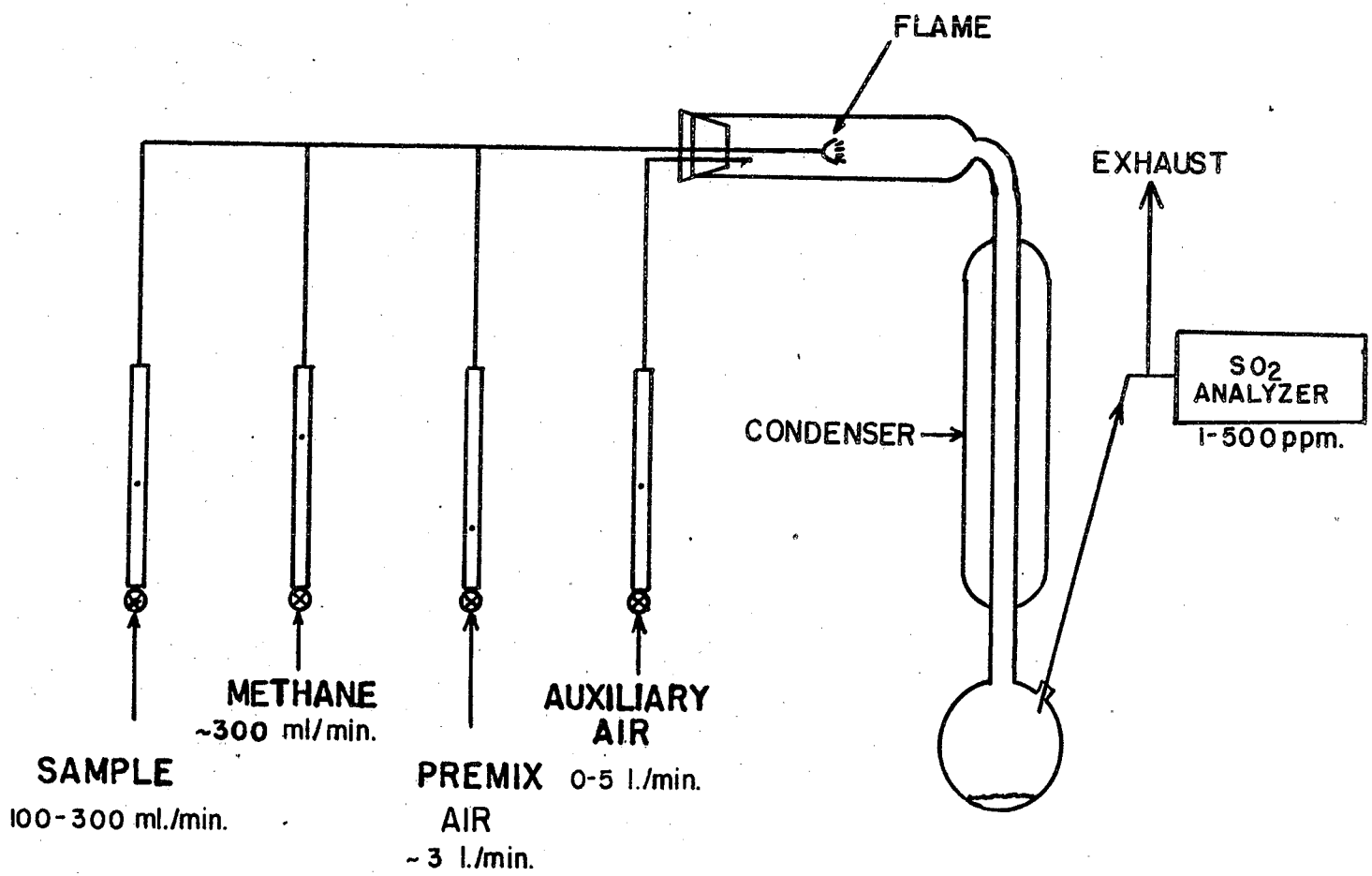


FIGURE 6-2

Laboratory device for testing a flame as a sulfur converter

lighting the flame in open air, and then introducing it gradually into the burner chamber. Although a flame could easily be maintained in open air, it proved difficult at first to introduce the flame into the closed system without extinguishing it. A stable enclosed flame was finally achieved by balancing the flow rates of methane, sample, and air such that the gas velocity at the burner jet was slightly larger than the flame velocity. This could be achieved at the nominal flow rates listed in the figure, although it was often helpful to adjust the methane and air flow rates slightly to achieve a conically-shaped, blue flame. When operated properly, the flame was almost invisible and best seen in subdued light. Once the flame was enclosed it could still be extinguished by sudden changes in downstream pressure, resulting from attaching the receiving flask to the exhaust line. However, models of this device which have been assembled subsequently for field monitoring exhibited more stable and more easily ignited flames. This improvement was achieved by using small diameter (1/8") tubing for the gas supply lines, for which slight pressure fluctuations are less likely to cause flow disruptions, and by including a valve downstream from the condenser which could be closed gradually once the flame was lit and enclosed. With such modifications the flame can normally be lit externally to the system and enclosed without extinguishing it. It was observed that small leaks in the feedthrough to the combustion chamber resulted in less stable flames and more difficulty in enclosing the flame. It is thus important that the feedthrough be an air-tight seal.

The conversion efficiency for seven different S gases was determined for concentrations ranging from 283-34,000 ppmv. Both $H_2$ and $N_2$ were used as diluent gases in preparing the standards to simulate both lean (direct mode) and rich (indirect mode) retort gases. Table 6-1 shows that the conversion efficiency is essentially 100% within the precision of the method. The single

Table 6-1

CONVERSION OF VARIOUS S COMPOUNDS TO $SO_2$ IN FLAME CONVERTER

| S Species | Carrier Gas | Concentration of S Species (ppmv/v) | % Conversion to $SO_2$ |
|---|---|---|---|
| $H_2S$ | $N_2$ | 34,000 | 102.5 |
| $H_2S$ | $N_2$ | 15,800 | 96 |
| $H_2S$ | $N_2$ | 7,000 | 98 |
| $H_2S$ | $N_2$ | 2,000 | 106 |
| $H_2S$ | $N_2$ | 1,184 | 98.4 |
| $H_2S$ | $N_2$ | 536 | 105.6 |
| $H_2S$ | $N_2$ | 283 | 23 |
| $H_2S$ | $H_2$ | 26,570 | 93 |
| $H_2S$ | $H_2$ | 12,435 | 98 |
| $H_2S$ | $H_2$ | 4,174 | 101 |
| $H_2S$ | $H_2$ | 1,530 | 104 |
| $H_2S$ | $H_2$ | 1,180 | 108 |
| $H_2S$ | $H_2$ | 2,640 | 96 |
| $H_2S$ | $H_2$ | 9,130 | 101 |
| $H_2S$ | $H_2$ | 26,600 | 97 |
| $H_2S$ | $H_2$ | 1,820 | 104 |
| $H_2S$ | $H_2$ | 18,800 | 95 |
| $CH_3SH$ | $N_2$ | 4,000 | 98-100 |
| $CH_3SSCH_3$ | $N_2$ | 1,960 | 101 |
| $CH_3SSCH_3$ | $N_2$ | 980 | 102 |
| Thiophene | $N_2$ | 2,220 | 100 |
| Thiophene | $N_2$ | 1,110 | 101 |
| COS | $N_2$ | 3,200 | 97 |
| COS | $N_2$ | 26,000 | 92 |
| COS | $N_2$ | 16,000 | 100 |
| $CS_2$ | $N_2$ | 7,250 | 96 |
| $CS_2$ | $N_2$ | 2,900 | 98 |
| $CS_2$ | $N_2$ | 1,450 | 95 |
| $SO_2$ | $N_2$ | 1,430 | 99 |

low conversion efficiency for $H_2S$ at 283 ppmv is due to baseline drift in the $SO_2$ monitor. For this run the sample was diluted 70 fold, resulting in an $SO_2$ concentration of approximately 4 ppmv, which is near the detection limit of the $SO_2$ monitor used in this experiment. Since the total S content of retort gas is typically within the range tested in this experiment, these data indicate that the methane/air flame is an efficient device for non-selectively converting the various S species in retort gas to $SO_2$. While this device could also be used at concentrations lower than those shown in the table, further testing should be performed before applying this method to gases containing less than 500 ppmv of total S.

Although data in Table 6-1 do not indicate an effect due to the sample matrix, a minor effect can be expected, as illustrated by the following calculation: assuming that essentially 100% of the S species are converted to $SO_2$, the resulting $SO_2$ concentration depends on both the flow rate of the sample into the flame and the total flow rate of gas to the $SO_2$ monitor. However, to a small extent the total flow rate of combusted gas to the monitor, $Q_c$, depends on the components of the sample gas. For example, one mole of $H_2$ in the sample reacts with ½ mole of $O_2$ to form one mole of $H_2O$, which is removed by the condenser. Thus, introducing 100 ml/min of $H_2$ in the sample causes the loss of 50 ml/min in total flow. On the other hand, CO in the sample causes a net increase in $Q_c$

$$CO + \tfrac{1}{2}O_2 \longrightarrow 2\ CO_2$$

Thus, 4,000 ppmv of $H_2S$ in $H_2$ would give a slightly higher response at the $SO_2$ monitor than would 4,000 ppmv of $H_2S$ in CO. Such differences are minimized primarily by maintaining a total flow rate approximately 40 times higher than the sample flow rate. Errors of this type are considered in Appendix 6A for a range of retort gases. Under worst case conditions (e.g., using a standard of

$H_2S$ in $N_2$ for monitoring a direct mode retort gas) an error of 5% could be incurred. Thus, for best results a standard should be selected which resembles somewhat the gas to be analyzed. For example, choosing a $N_2$-based standard for the analysis of direct-mode retort gases would produce errors of approximately 0.5%. Thus, by using a reasonable standard, and by keeping the auxiliary air, premix air and methane flow rates constant between sample and standard, the concentration of S in the sample is given by the expression (Appendix 6A):

$$(1) \qquad (S)_{RG} = (S)_{STD} \frac{(SO_2)_{RG}}{(SO_2)_{STD}} \frac{Q_{STD}}{Q_{RG}}$$

Where:

$(S)_{RG}$ = total concentration of S in the retort gas on a dry basis

$(S)_{STD}$ = concentration of S in the standard on a dry basis (ppmv)

$(SO_2)_{RG}$ = concentration of $SO_2$ produced by the retort gas during combustion (ppmv)

$(SO_2)_{STD}$ = concentration of $SO_2$ produced by the standard during combustion (ppmv)

Since $SO_2$ is measured by the pulsed fluorescent analyzer and $(S)_{STD}$ is known, $(S)_{RG}$ is readily calculated. The absolute value of $(SO_2)$ need not be known, but only some value in proportion. Thus, the $SO_2$ analyzer need not be calibrated against an $SO_2$ standard, but rather against any standard containing an S species. This feature of equation 1 greatly simplifies the calibration procedures. Although equation 1 is generally applicable, the analyst should be aware of the assumptions and limitations inherent in its derivation, as detailed in Appendix 6A.

Because of the encouraging results obtained in the laboratory, a total S system was assembled and tested under field conditions courtesy of an opportunity provided by the Laramie Energy Technology Center. This test was carried

out in conjunction with the September 8-15, 1980 operation of the 150 ton retort at the North Site Test Facility of the LETC. The apparatus assembled for this purpose was similar to the device shown in Figure 6-2. It was designed to operate for a short period in the mobile laboratory which was on site at the time, but was not sufficiently rugged for long term, routine application. Changes in the device included an improved, positive seal feed through and the incorporation of the combustion chamber into the end of the condenser. The primary purpose of this test was to determine the mechanical and pneumatic integrity of the analyzer, not to provide monitoring data for the retort.

However, to deal with actual retort gases several more substantive changes were required in peripheral equipment. The retort gas being tested contained suspended matter and was saturated with water and possibly oil at approximately 60°C and could not be introduced directly into the total S analyzer without certain precautions. Similar gases from other industrial sources are cooled to remove water and oils. However, in the case of retort gas such treatment could result in the loss of sulfur compounds, and efforts were therefore made to avoid this treatment. Instead of cooling the gas, all sampling parts which were exposed to retort gas were heated to approximately 70°C. Suspended matter was removed by an in-line filter. Since the response of the total S analyzer is proportional to the sample flow rate, the sample rotameter was replaced with a mass flow meter to obtain more precise and accurate flow measurements. Since response of the mass flow meter to retort gas would likely be different than its response to the standard gas, provisions were included to calibrate the mass flow meter for each type of gas.

The entire flow scheme, including facilities for sampling, sample conditioning, combustion, calibration and analysis is shown in Figure 6-3.

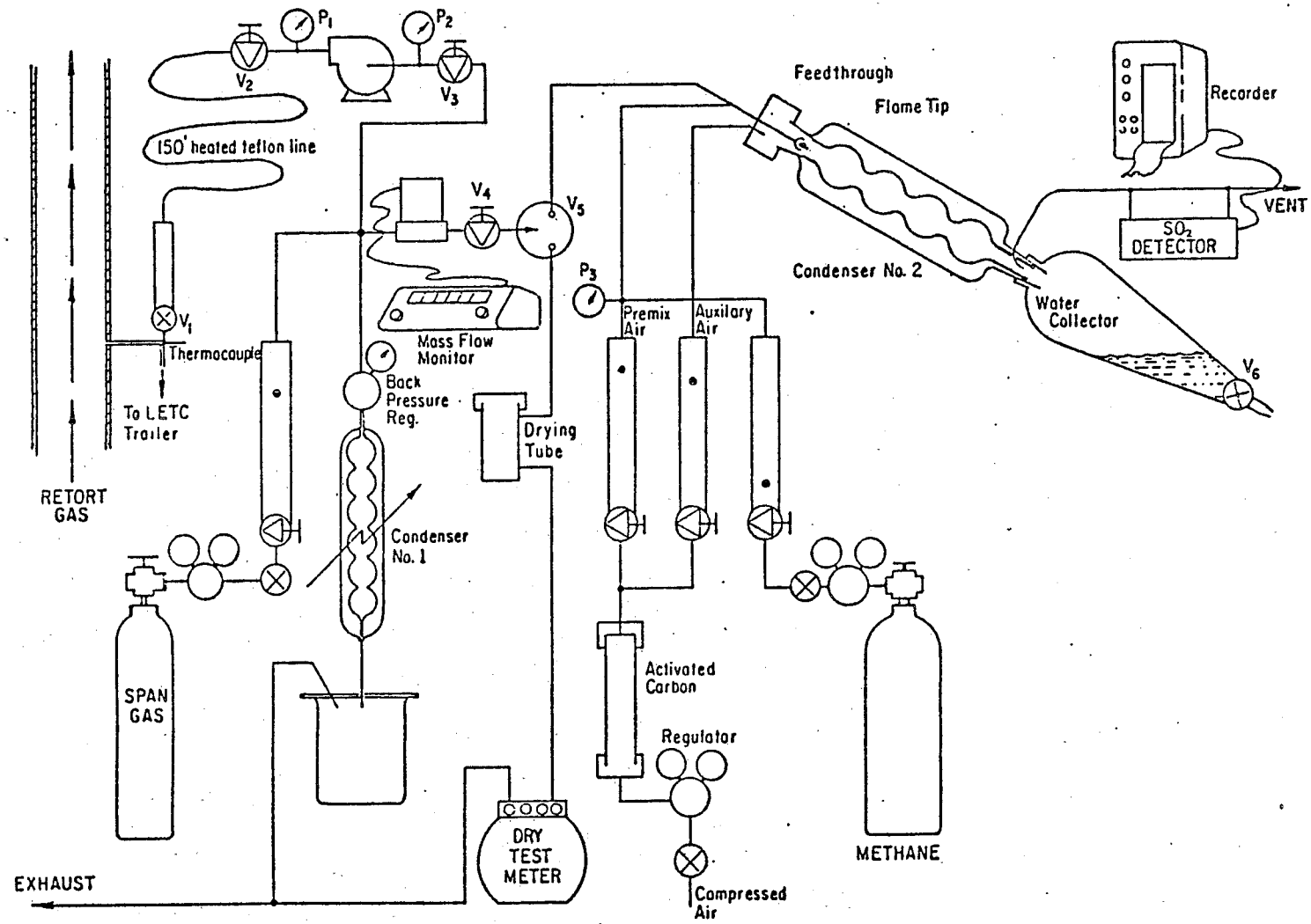


FIGURE 6-3

Total sulfur system operated during the fall, 1980 field test

In order of occurrence, the gas exited the process gas line through a port which was shared with LETC, passed through a glass fiber filter cartridge (Balston Corp.), and moved to the sampling trailer through 150 feet of Teflon-lined hose which was heated to 70°C. The flow of retort gas through the sample line was controlled by valve V2 at approximately two liter minute$^{-1}$. At this rate, transit time in the sample line was approximately one minute. The pressure downstream from the sample pump was maintained at approximately 4 psi with a back pressure regulator to provide a constant pressure for metering valve $V_4$, which regulated the flow of gas to the combustor.

The dry test meter in Figure 6-3, with the drying tube and valve V5, was included to calibrate the mass flow monitor. Although the mass flow monitor is relatively insensitive to temperature and pressure, its response is proportional to the specific heat of the gas. In theory, then, the mass flow monitor could be calibrated either volumetrically or by measuring the specific heat of the sample gas.

To operate this device the air and fuel flows were first started (with V2 off), the flame was lit and introduced into the chamber and the $SO_2$ analyzer was zeroed. The span gas was introduced next with the flame burning burning, V4 was adjusted to admit approximately 100 ml/min to the burner, and the span of the $SO_2$ detector adjusted. Leaving the air and fuel rates constant, the span gas was stopped, V2 was opened enough to admit approximately 2 liter min$^{-1}$ of retort gas, and V4 was adjusted again, if necessary, to admit approximately 100 ml of retort gas to the flame. The concentration of total S was then calculated according to equation 1.

During this test the total S analyzer (TSA) was operated from 16:43 on 9/13/80 until the end of the retorting operation at 00:13 on 9/18/80. This allowed for observation of changes in S concentrations on a real-time basis

during much of this period and also provided valuable information on the operation of the analyzer.

Operating parameters were initially set as follows and were left constant except for minor changes in sample flow to the combustor.

| | |
|---|---|
| Flow rate in sample line | 2 al $min^{-1}$ |
| Premix air flow | 0.8 al $min^{-1}$ |
| Auxiliary air flow | 3.1 al $min^{-1}$ |
| Methane flow | 90 aml $min^{-1}$ |
| Pressure at back pressure regulator | 4 psi |
| Pressure at burner (gauge P3) | 0 (atmospheric) |
| Mass flow meter reading for standard | 083 std ml/min |
| Mass flow meter reading for sample | 125 std ml/min |
| Temperature of sample line | 165°F |
| Temperature of mass flow meter, sensing head, and other components exposed to retort gas | 150°F |
| Span gas, $CH_3SH$ in $N_2$ | 4000 ppm v |
| Burner head | quartz w 7 mm ID at tip |

All parameters were identical for both sample and standard except sample flow rates through the mass flow meter, which varied as indicated.

The TSA first operated with span gas and was then switched to retort gas. Stable operation was observed in both cases. The flame burned well in the enclosed combustion chamber and produced readings which were stable, reasonable and well within the working range (1-5,000 ppmv) of the $SO_2$ analyzer. However, no independent measurements of S species were available for comparison.

The next step was to have been calibration of the mass flow meter with the dry test meter. However, this operation was not performed during this test

because of the unexpectly high level of oily materials in the retort gas which could have resulted in fouling and poor operation of the dry test meter. Instead, calibration factors were calculated based on the concentrations of the major gas components (Appendix 6B). In the future a bubble meter could provide a simpler and more rugged method of calibrating the mass flow meter.

Once measurement of the retort gas began (16:55 on 9/13/80), the analyzer ran continuously until the end of the burn although the recorder was operated only intermittently. It was apparent that S levels were essentially constant during this period. The response time for the complete sampling and analysis system, including 150' of sampling line, could also be estimated during this period. From the time the retort gas was first allowed into the sampling line until the $SO_2$ analyzer achieved full response required 4 minutes.

During the evening of 9/13 to 9/14 the most serious malfunction of the test occurred. The temperature controller for those parts of the system exposed to retort gas malfunctioned, allowing the temperature to increase to 100°C. This temperature is well above the rating for the mass flow meter, and readings from this device were erratic thereafter. For this reason concentrations reported for periods after 9/13/80 should be considered less reliable.

Total S concentrations were calculated using equation 1, and results follow:

| Date | Time | S (ppmv, dry basis) |
|---|---|---|
| 9/13/80 | 16:55-18:18 | 3,700-4,000 |
| 9/14/80 | 07:30-07:51 | 3,800-3,400 |

While the monitoring data obtained during this test was meager, the information gained on instrumental requirements of a practical total S monitor was substantial. Most failures in the tested system were related to its

inability to tolerate a realistic retort gas sample. A discussion of the shortcomings of the system tested during this period and possible solutions follow:

1. During this test the components exposed to retort gas were traced with heating tapes to keep them above the dew point of the retort gas. In view of the amount of condensation which occurred, it would appear to be necessary to keep all exposed components in a temperature controlled chamber at 110°C or more, above the boiling point of condensible materials.
2. To use a mass flow monitor at 110°C, a special high-temperature model is required. Using a mass flow monitor is questionable since the sensing element of this device consists of a small diameter tube through which a portion of the gas must pass. It would seem that such a sensing element is inherently inappropriate for retort gas, and that retort gas should be controlled by devices which do not need small, easily plugged orifices.
3. A better approach would avoid using untreated retort gas either by developing a method of treating the gas which can be shown not to cause changes in composition, or by diluting the gas with a pure carrier to lower its dew point to below room temperature. One practical approach to the latter would be volumetric dilutors which are now commercially available but have not been tested under this program. Such devices operate by adding known, fixed volumes of a sample gas to a continuously flowing diluent gas stream. Metering of sample gas by fine control valves, rotameters, or mass flow meters, all of which are easily fouled by retort gas, would not be required.

4. The dry test meter shown in the figure for calibrating the mass flow meter is too easily contaminated and too difficult to clean. A simpler device, such as a bubble meter, would be more appropriate.
5. The lines for the sample and span gas should be better separated than in Figure 6-3. This design wastes span gas through the back pressure regulator and also contaminates the span gas line with retort gas. The mechanical back pressure regulator did not work entirely satisfactorily, generating back pressure changes when the flow rate changed. A column of water would appear to be more reliable and practical as a back pressure regulator.
6. Condenser #2 in Figure 6-3 should be replaced with a permeable membrane dryer to avoid the need for a recirculating cooling bath.
7. In spite of the in-line filter and the elevated temperature of the sampling line, condensed material was found in the sampling line and filter holder. Future designs should thus include a better means of protection, such as more efficient filters or traps.

In summary, this preliminary test of the total S analyzer indicated several mechanical and instrumental problems. In retrospect, these problems appeared amenable to straight forward solution. More importantly, the basic operating principles of the system appear sound.

At this point in time it was considered that the principles of a total S measurement had been established, and further work was not required under this EPA contract. However, further funding was made available from the Laramie Energy Technology Center (DOE) to provide total S measurements in support of their field testing program (Contract No. DE-AS20-81LC0771). This provided an opportunity to assemble and operate a total S analyzer including some of the suggested modifications.

The system designed for this purpose was similar to the original laboratory model with modifications to improve reliability and portability (Figure 6-4). Prior to introduction into the instrument, the retort gas was cooled, dried, and filtered in order to improve ease of handling. The flow of retort gas and standard was monitored with a rotameter rather than a mass flow meter, an approach which proved to be considerably more reliable than the mass flow meter used in the previous experiment. Because the calibration of the rotameter was expected to be different for the standard and sample gases, an in-line bubble meter was included for calibration. The calibration of the rotameter for dried, cooled retort gas from the direct mode processes which have been monitored has not differed measurably from the calibration of the standard. However, such would not necessarily be the case for different types of sample gas. Unlike the laboratory model, this model used a DuPont Model 411 monitor, a uv absorption instrument to detect the $SO_2$ produced by the flame. This instrument has an unexpected advantage in as much as the cell operates at slightly elevated temperatures (approx. 40°C) so that the condenser need not be as efficient at removing water vapor as the laboratory model. Unlike the laboratory model, this model included a cartridge of granular $PbCO_3$ which could be switched into the sample line periodically. The purpose of this cartridge was to selectively remove $H_2S$ to measure "non-$H_2S$" sulfur species in retort gas. When challenged with several 1,000 ppmv of $H_2S$, this cartridge removed all measurable amounts. However, its effect on other S species has not yet been established comprehensively. The pressure switch shown is included to turn off the methane flow in the event of a failure in the air or power supply.

The main problem with the total S analyzer, as shown in Figure 6-4, is the need for almost constant operator attention. Because the $SO_2$ monitor is being operated near its detection limit (approx. 5 ppmv), the operator is required to

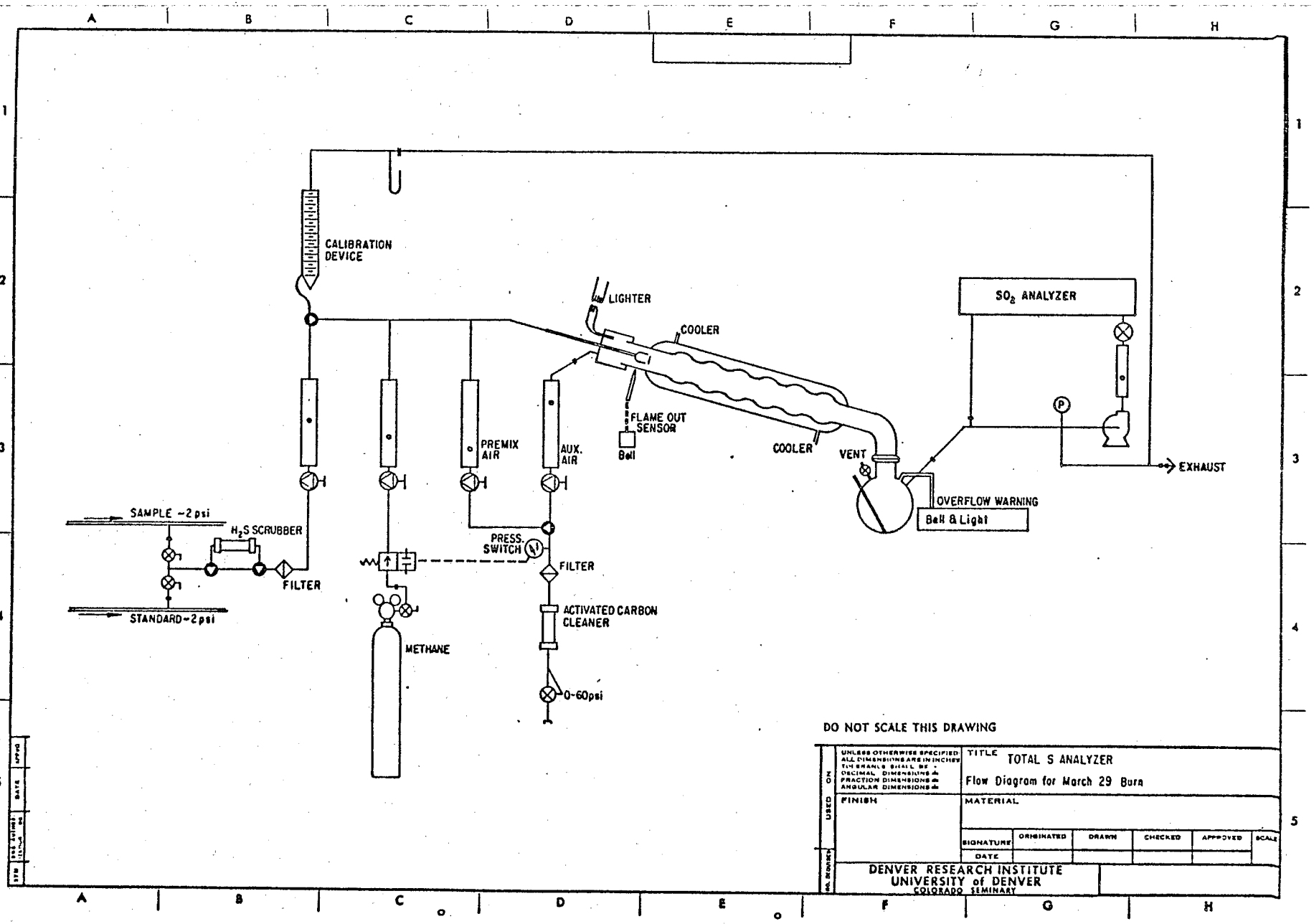


FIGURE 6-4

Total S analyzer

check the zero and span approximately once per hour, in addition to switching between the various samples which are being monitored.

In the device shown, the inlet flow rate of sample and standard depends on the pressure in the sample and standard lines. For best results the operator must therefore monitor and adjust the flow rate through the sample rotameter. Pressure fluctuations are naturally occurring in the process line and are transmitted to the sample line which in turn affects the flow to the analyzer. This effect has been minimized but not eliminated by using in-line regulating devices such as mechanical pressure regulators and water columns. Although the rotameter is more reliable than the mass flow meter, it still must be removed and cleaned every few days. These problems, while causing an inconvenience, are easily corrected: the reliability of the gas metering could be improved through the use of a volumetric dilution system as discussed previously. The frequent switching between standards and various samples could be performed easily by an automated sequence of solenoid valves. The drifting of the $SO_2$ monitor, which is associated with operation near the detection limit, could be eliminated by using a more sensitive monitor.

To check the operation of the total S analyzer, total S measurements have been made simultaneously with the measurement of $H_2S$, COS, $CS_2$, and methyl mercaptan by gas chromatography at the North Site Test Facility of the Laramie Energy Technology Center. The sum of these individual gases measurements was normally slightly lower than the total S measurement. However, total S results were occasionally up to 10% lower than the summation, indicating a need for improving the precision of one or both of these techniques. Nevertheless, total S measurements were clearly achievable with the method discussed and implementation of the improvements suggested should make this method more reliable.

## APPENDIX 6A

## DERIVATION OF THE CALIBRATION FORM FOR S ANALYZER

Since the combusted gas is dried prior to the $SO_2$ analyzer, all results from the monitor are on a dry basis. In the following discussion, all symbols for gas concentration will be on a dry basis unless otherwise noted.

The $SO_2$ concentration at the analyzer ($SO_2$) is given by the ratio of the flow rate of S compounds into the flame divided by the flow rate of the dry combusted gas. Consider first the volume of dry gas produced in the absence of any sample. Because of the combustion of methane,

(1) $$CH_4 + 2O_2 = CO_2 + 2\,H_2O$$

the volumetric flow rate of the combusted gas, $Q_c$, is given by

(2) $$Q_C \cong Q_A - Q_{O_2} + Q_{CO_2} = Q_A - 2Q_M + Q_M$$

$$Q_C = Q_A - Q_M$$

where $Q_C$ = volumetric total flow rate of the combusted gas, dry basis

$Q_A$ = volumetric total flow rate of air into the combustion chamber

$Q_M$ = volumetric total flow rate of methane

$Q_{O_2}$ = volumetric total flow rate of $O_2$

$Q_{CO_2}$ = volumetric total flow rate of $CO_2$

For the flow rates described in the main text, $Q_C$ is therefore approximately 3,900 ml/min. When standard gas is introduced in the form of 4,000 ppmv $CH_3SH$ in $N_2$ at flow rate $Q_{STD}$, total flow rate is increased by essentially the same amount:

(3) $$Q_C = Q_A - Q_M + Q_{STD}$$

where STD denotes standard.

The concentration of $SO_2$ in the combusted gas (in ppmv) is then

$$(4) \qquad (SO_2)_{STD} = \frac{Q_{STD}(S)_{STD}}{Q_A + Q_{STD} - Q_M}$$

where $(S)_{STD}$ is the S concentration in the standard.

When the sample is introduced in place of the standard, the degree to which $Q_C$ is altered depends somewhat on the composition of the sample. Water vapor will pass through the flame and be collected in the condenser. Hydrocarbons and $H_2$ will remove a fraction of the $O_2$ supplied by the combustion air. $N_2$ and $CO_2$ will pass through the flame unaffected. Table 6A-1 summarizes the reactions which can be expected for typical retort gases, along with the consumption and production of combusted gas.

For the MIS retort gas shown, the flow rate of dry combusted gas is therefore:

$$(5) \qquad Q_C = Q_A - Q_M + (0.965 - 0.130)\, Q_{RG}$$

where the subscript RG denotes retort gas.

The concentration of $SO_2$ in the combusted sample stream is thus:

$$(6) \qquad (SO_2)_{RG} = \frac{Q_{RG}(S)_{RG}}{Q_A + 0.835\, Q_{RG} - Q_M}$$

Combining equations 4 and 6 thus gives the concentration of S in the retort gas.

$$(7) \qquad (S)_{RG} = (S)_{STD} \frac{(SO_2)_{RG}}{(SO_2)_{STD}} \frac{Q_{STD}}{Q_{RG}} \frac{Q_A + 0.835\, Q_{RG} - Q_M}{Q_A + Q_{STD} - Q_M}$$

By adjusting the flow rates $Q_{RG}$ and $Q_{STD}$ to approximately the same value, the last term in equation 7 becomes unity within experimental error, as illustrated by considering typical values for the various flow rates: $Q_A$ = 4,000 ml/min; $Q_{RG} = Q_{STD}$ = 100 ml/min; $Q_M$ = 100 ml/min. For these rates, the last term in equation 7 is 0.9959.

Table 6A-1

PRODUCTION OR CONSUMPTION OF GASES DURING COMBUSTION

| Component | %,v/v | Reaction | $O_2$* Consumed (%,v/v) | Dry Gas* Produced (%,v/v) |
|---|---|---|---|---|
| ----------MIS RETORT GAS---------- | | | | |
| $N_2$ | 57.7 | -- | 0.00 | 57.7 |
| $CO_2$ | 32.0 | -- | 0.00 | 32.3 |
| CO | 1.0 | $CO + 1/2\ O_2 = CO_2$ | 0.5 | 1.0 |
| $H_2$ | 5.5 | $H_2 + 1/2\ O_2 = H_2O$ | 2.8 | 0.0 |
| $CH_4$ | 1.5 | $CH_4 + 2\ O_2 = CO_2 + 2\ H_2O$ | 3.0 | 1.5 |
| $C_2H_6$ | 0.4 | $C_2H_6 + 7/2\ O_2 = 2\ CO_2 + 3\ H_2O$ | 1.4 | 0.8 |
| $C_3H_6$ | 0.3 | $C_3H_6 + 9/2\ O_2 = 3\ CO_2 + 3\ H_2O$ | 1.4 | 0.9 |
| $C_4H_{10}$ | 0.4 | $C_4H_{10} + 13/2\ O_2 = 4\ CO_2 + 5\ H_2O$ | 2.6 | 1.6 |
| $O_2$ | 0.1 | -- | -- | 0.1 |
| $H_2S$ | 0.3 | $H_2S + 3/2\ O_2 - SO_2 + H_2O$ | 0.5 | 0.3 |
| $NH_3$ | 0.8 | $NH_3 + O_2 = 1/2\ N_2 + 3/2\ H_2O$ | 0.8 | 0.4 |
| TOTAL | 100.0 | | 13.0 | 96.50 |
| ----------TOSCO RETORT GAS---------- | | | | |
| $H_2$ | 22.5 | $H_2 + 1/2\ O_2 = H_2O$ | 22.5 | 0 |
| $CH_4$ | 15.2 | $CH_4 + 2\ O_2 = CO_2 + 2\ H_2O$ | 30.2 | 15.2 |
| CO | 3.8 | $CO + 1/2\ O_2 = CO_2$ | 1.9 | 3.8 |
| $H_2S$ | 4.3 | $H_2S + 3/2\ O_2 = SO_2 + H_2O$ | 6.5 | 4.3 |
| $CO_2$ | 21.4 | -- | 0 | 21.4 |
| $C_2H_4$ | 5.4 | $C_2H_4 + 3\ O_2 = 2\ CO_2 + 2\ H_2O$ | 16.2 | 10.8 |
| $C_2H_6$ | 10.4 | $C_2H_6 + 7/2\ O_2 = 2\ CO_2 + 3\ H_2O$ | 36.4 | 20.8 |
| $C_3H_6$ | 3.7 | $C_3H_6 + 9/2\ O_2 = 3\ CO_2 + 3\ H_2O$ | 18.5 | 11.1 |
| $C_3H_8$ | 4.0 | $C_3H_8 + 5\ O_2 = 3\ CO_2 + 4\ H_2O$ | 20.0 | 12.0 |
| $C_4H_{10}$ | 4.2 | $C_4H_{10} + 1/3\ O_2 = 4\ CO_2 + 5\ H_2O$ | 27.30 | 16.8 |
| $C_5H_{12}$ | 2.5 | $C_5H_{12} + 8\ O_2 = 5\ CO_2 + 6\ H_2O$ | 20.00 | 12.5 |
| $C_6H_{14}$ | 1.5 | $C_6H_{14} + 9.5\ O_2 = 6\ CO_2 + 7\ H_2O$ | 14.3 | 9.0 |
| $C_7H_{16}$ | 0.8 | $C_7H_{16} + 11\ O_2 = 7\ CO_2 + 8\ H_2O$ | 8.8 | 5.6 |
| $C_8H_{18}$ | 0.3 | $C_8H_{18} + 12.5\ O_2 = 8\ CO_2 + 9\ H_2O$ | 3.8 | 2.4 |
| TOTAL | 100.0 | | 226.4 | 145.7 |

* volume consumed or produced per 100 ml of dry retort gas

Thus, for the MIS gas, the concentration of total S on a dry basis is given, within experimental error, by

$$(8) \qquad (S)_{RG} = (S)_{STD} \frac{(SO_2)_{RG}}{(SO_2)_{STD}} \frac{Q_{STD}}{Q_{RG}}$$

Since only relative concentrations of $SO_2$ are important, the $SO_2$ analyzer need not be calibrated separately and a single standard of, for example, $CH_3SH$ in $N_2$ is adequate.

Equation 8 remains an accurate simplification of equation 7 as long as the standard is reasonably similar to the sample gas. For example, for the field test described in this chapter, $CH_3SH$ in $N_2$ proved adequate for the measurement of MIS retort gas. However, significant error may be introduced by using an entirely inappropriate standard.

Suppose, for example, that the standard of $CH_3SH$ in $N_2$ were used for measurement of a high-heat-content gas, such as that produced by the TOSCO process. In this case (see Table 6A-1) the last term in equation 7 becomes:

$$(9) \qquad R = \frac{Q_A - 0.807\ Q_{RG} - Q_M}{Q_A + Q_{STD} - Q_M}$$

assuming that the standard is still contained in $N_2$. Using the same flow rates as above, R = 0.95, equation 8 could not be used without introducing a 5% error. If the gas composition is known, R could be calculated. However, a more reliable approach would be to use a standard which more closely approximates the sample. For TOSCO retort gas, for example, one could use $H_2S$ in methane, in which case R becomes:

$$R = \frac{Q_A - 0.807\ Q_{RG} - Q_M}{Q_A - Q_{STD} - Q_M}$$

For the flow rates used above, R then becomes 1.005 and equation 8 can be used without loss in accuracy.

In summary, equation 8 can be used without the loss of accuracy as long as the standard is vaguely similar to the sample. The effect of dissimilar standards can be calculated from equation 9. For the examples considered, an error of up to 5% could be introduced by use of an entirely inappropriate standard. Equation 8 also assumes that $Q_A \geq 40\ Q_{RG}$, which corresponds to approximately a two fold excess of air over what is needed for stoichiometric combustion of the sample and methane. Equation 8 is valid only if $Q_A$ and $Q_M$ remain unchanged between sample and standards.

## APPENDIX 6B

## CALIBRATION OF THE MASS FLOW METER

The response, r, of the mass flow meter is given by:

(1) $$r = kC_p Q$$

where k = constant depending on the meter design

$C_p$ = specific heat at constant pressure (cal $g^{-1}$)

p = density of gas (g/l)

Q = flow rate under standard conditions (ml/min)

The meter has been calibrated for $N_2$, so that $k = (1/C_p\rho_o)N_2$ where $\rho_o$ is the density of $N_2$ at standard conditions. Thus, for $N_2$

$$\frac{(\rho)}{(\rho_o)} Q_{N_2} = r_{N_2}.$$

The reading of the mass flow meter thus gives the flow rate of the span gas ($CH_3SH$ in $N_2$) in ml $min^{-1}$ adjusted to standard conditions.

The sensitivity of the mass flow meter for retort gas can be calculated from a knowledge of its composition. Note that the term $C_p\rho$ is the heat capacity in cal $deg^{-1}$ $liter^{-1}$. For a gas mixture under standard conditions, $C_p\rho_o$ the heat per liter is given by:

(2) $$C_p\rho_o = \frac{1}{100\ V_o} \Sigma\ c_p\ V$$

where $V_o$ = molar volume at standard conditions = 22.41

$C_p$ = molar heat capacity (cal $deg^{-1}$ $mole^{-1}$)

V = concentration (vol %)

The concentrations of the major gas components were provided by personnel from LETC, and the term $C_p$ is calculated as follows:

| Component | (vol %) | (Cρ) | |
|---|---|---|---|
| $H_2$ | 4.2 | 6.78 | 0.289 |
| $N_2$ | 46.1 | 6.94 | 3.198 |
| CO | 1.8 | 6.94 | 0.125 |
| $CH_4$ | 1.1 | 8.45 | 0.093 |
| $CO_2$ | 20.5 | 8.75 | 1.794 |
| $H_2O$ | 25.0 | 8.68 | 2.169 |
| other | 1.3 | 11.58 | -- |
| | | | 7.667 |

$$(C_p\rho_o) = 0.342 \quad \text{cal deg}^{-1}\ \text{l}^{-1}$$

The response of the mass flow meter to retort gas is thus given by:

(3) $$r_{RG} = \frac{(C_p\rho_o)_{RG}}{(C_p\rho_o)_{N_2}} \frac{(\rho)}{(\rho_o)} Q'_{RG} = \frac{(.342)}{(.310)} \frac{(\rho)}{(\rho_o)_{RG}} Q_{RG} = 1.10 \frac{(\rho)}{(\rho_o)} Q'_{RG}$$

where $Q'_{RG}$ is the flow rate on a wet basis. Since the flow rate on a dry basis is needed,

(4) $$\frac{(\rho)}{(\rho_o)_{RG}} Q_{RG} = \frac{(1\text{-}\%\ H_2O)}{100} \frac{1}{1.10} r_{RG} = 0.679\ r_{RG}$$

In summary, considering only flows at standard conditions, as denoted by the "o" superscript,

(4) $$Q^o_{STD} = r_{STD}$$

and

$$Q^o_{RG} = 0.679\ r_{RG}$$

where the subscript STD and RG denote the standard and retort gas, and all flows are on a dry basis.

## SECTION 7

## SULFUR SPECIES IN RETORT GAS

Several writers have suggested that atmospheric sulfur emissions could be the environmental factor which limits the eventual size of the oil shale industry. Sulfur control technology is thus crucial to the oil shale industry, and it is advantageous to consider various types of control technologies. However, proper selection of a sulfur centrol technology requires a knowledge of the S species which are present in the retort gas. For example, $H_2S$ is normally removed by oxidizing processes, such as the Stretford process, which are ineffective with other types of sulfur compounds. $SO_2$ is most frequently removed by alkaline agents, which are not necessarily effective for other components. Reliable methods of analysis for sulfur species in retort gas are clearly required.

In order to understand the role of sulfur speciation in the development of sulfur control technology, the overall plant design must be considered. Present development plans call for combustion of the retort gas to produce heat. As such, various sulfur species would be emitted as their combustion product, $SO_2$. Thus, one option to sulfur control is the use of flue gas desulfurization systems, such as alkaline scrubbers. However, it is usually preferable to remove the sulfur from the lower volume uncombusted fuel gas, where higher control efficiencies can often be obtained at lower cost. In this context methods for sulfur speciation are required, not for regulatory purposes, but for the selection and testing of retort gas desulfurization systems.

The objective of the efforts described in this chapter is thus to develop a method or methods appropriate for determining major and minor sulfur species

in retort gas. These methods must necessarily be sufficiently rugged for use on site in a field laboratory and must yield results rapidly enough to permit the operator to optimize plant conditions.

The characteristics of the gas which must be analyzed depends principally on the retorting process. Two major categories of retort gases are recognized: (1) low heat-content gases, which are produced by processes which introduce air directly into the retort (direct processes), and (2) high heat content gases, which are produced by retorts which exclude air from the retort. The indirect process gases consist primarily of $H_2$, $CH_4$, $CO_2$, CO, and $C_1$ to $C_4$ hydrocarbons. The direct process gases are of similar composition but are diluted with approximately 60-70% $N_2$ and 20% $CO_2$. Both gases are saturated with water vapor and hydrocarbons and may contain suspended oil and water droplets and particulate matter. $NH_3$ may be present in amounts which depend on the retorting process. At the start of this project it was recognized that $H_2S$ was a major sulfur species, although the contribution of other species such as COS, $SO_2$, $CS_2$, and $CH_3SH$ was uncertain.

It was clear at the outset of this project that whatever method was developed for sulfur speciation must be tolerant of high levels of the contaminant gases and water vapor. While it must be capable of monitoring $H_2S$ routinely, it must also be flexible enough to monitor the several other sulfur species which had not yet been determined.

The approach used for this problem was gas chromatography with a flame photometric detector (GC/FPD). Several columns were evaluated and are described below in order that the analyst can select the most appropriate columns as he gains more information regarding the most important sulfur species.

GC/FPD has been applied widely and is much discussed in the literature. Here we mention only the most relevant citations, discussing first the FPD and then the columns. A more complete survey has been provided by Wallace (1981).

The characteristics of the FPD have been reported extensively in the literature (Stevens et al., 1971; Lucero and Palzing, 1974; Bradey and Chaney, 1966). Salient features include

1. A dynamic range of $10^{-10}$ to $10^{-7}$ g/sec
2. A response proportional to $S^n$, where n is normally close to 2.0 but depends on the molecular form of the S
3. Freedom from reagent requirements except for compressed gases
4. Fast response compared to most other S detectors
5. Instability of the flame upon exposure to combustible gases such as $H_2$, CO, and hydrocarbons, or upon sudden changes in gas flow
6. Selectivity ratios for S compounds (as compared to hydrocarbons) of up to $10^4$
7. Suppression of the S signal by $CO_2$ or hydrocarbons

Several of these features are distinct advantages for field monitoring of S species. For example compressed gas requirements are normally minimal and could, in fact, be provided by an air compressor and $H_2$ generator in environments where compressed gases are not permitted for safety reasons. The fast response (item 4) means that this detector, unlike other S-selective detectors can be used with capillary columns. The detectability (item 1) is more than sufficient for retort gases which typically contain $H_2S$ in the range 1,000 to 50,000 ppmv. The dynamic range translates to approximately 500-20,000 ppmv with a 1 μl sample injection volume and a packed column. Present technology permits direct injection of sample volumes between 0.25 to 3,000 μl, enabling use of the FPD conveniently for S concentrations in the range 0.2 ppmv

to 8% v/v. However, for any given sample volume the dynamic range is approximately 500:1 and a wider range would be more convenient when trying to cover a range of concentrations with a single instrument.

The dependence of the FPD response on molecular form means that the GC must be separately calibrated for each gas. Especially in a field laboratory the preparation and handling of numerous gas standards is often more difficult than the analyses proper, and this feature of the FPD means that most analyses are carried out on only a few S species. Varian Associates has attempted to minimize this inconvenience by placing two flames in series, the first to combust all forms of S to common fragments and the second to provide the fluorescent signal. This arrangement was also designed to minimize flame extinction and hydrocarbon quenching. However, even with the dual flame detector, Gangwal et al. (1979), report that the FPD remains measurably sensitive to molecular form.

The instability of the flame arises from the requirement of operating the FPD with a fuel rich flame, often verging on extinction. After extinction the FPD typically must be recalibrated, resulting in the loss of valuable data. During the initial stages of this investigation it was uncertain whether retort gases contained sufficient combustible gases to extinguish the flame. This did not prove to be a problem. However, flame-out did often occur during valve switching until a flow regulator was installed between the column and detector.

The problem considered in most detail in this study was the possibility of the S signal being affected by co-eluting $H_2$, $CO_2$, or hydrocarbons found in retort gas. This effect has been reported in the literature, although not necessarily in terms that permit direct application to retort gas. For example, Von Lehmden (1978), reported up to 40% suppression of the FPD response when $CO_2$ was present in a thousand fold excess. The effect of $CO_2$ in retort

gas, which may reach levels of 20% v/v, was uncertain. Fluoresence quenching by hydrocarbons has been discussed by Patterson (1978), Sugiyama et al. (1973), and Thompson (undated). They observed that major amounts of hydrocarbons could entirely suppress the signal from a minor S species, (e.g., S in natural gas), although quantitative data for commercially available detectors was not available. The dual flame detector manufactured by Varian (Patterson, 1978; Thompson, undated) apparently minimized the quenching effect, although data was not available to quantitate its importance in retort gas.

Because some overlap of hydrocarbons and sulfur species inevitably occur, it was necessary to measure quantitatively the quenching effect of co-eluting hydrocarbons. For example, would 3% ethane in retort gas significantly distort the measurement of 300 ppmv $H_2S$? Because the dual flame detector offers apparent advantages while the single flame system is more common, both types of detectors were investigated and compared.

As with the detector, column material and design are also widely discussed in the literature. By way of summary, numerous column packings have been designed, each of which have been applied to a relatively small group (~ie, 2-4) of S compounds. However, in the absence of previous data the analysis of retort gas was complicated by the possible existence of over 20 possible compounds and isomers with 4 or less carbon atoms.

Packings described in the literature include silicone rubber (Martin and Grant, 1965), polyphenylether $+H_3PO_4$ on teflon (Stevens and O'Keefe, 1970), acetone-washed Porapak QS, one of the most popular columns (De Souza and Bhatia, 1976), silicone QFI 6,500 on Porapak QS (Pearson and Hines, 1977), Tenax GC (Walker, 1978), treated silica gel (Stetter, 1977), and Chromosil 107 (Sklarlew et al., 1981). The limitations of packed columns are typified by the procedures described by Pearson and Hines (1977), which they recommend for the

determination of $H_2S$, COS, $SO_2$, and $CS_2$ in hydrocarbon gases. For example, the total analysis requires 4 different columns. An alternative approach with a wall cooled open tubular column (WCOT) was described by Farwell (1979) which could separate most compounds with boiling points below 200°C. Disadvantages of the WCOT column, however, included the loss of $SO_2$ (one of the species of interest in retort gas), questionable separation of COS from large excesses of $H_2S$, and cryogenic column temperatures, which results in somewhat more complicated equipment.

Gas chromatography has also recently been applied to oil shale process gas. For example, Goodfellow and Atwood (1974) analyzed the gas from a Fischer assay for $H_2S$ using a GC technique. They achieved 95% elemental mass closure, which suggested that major analytical errors did not occur. Skogen (1980) has employed columns of 5% QF-1 and polyphenylether on Porapak QS for monitoring a modified in situ retort. While these reports deal with application of GC/FPD to retort gas, they do not include in-depth analyses of interferences and suppression effects.

Because of the detector characteristics, it is preferable that the GC column be capable not only of separating the constituent sulfur species from each other but also from the hydrocarbons in retort gas. Because of the numerous possible S species (greater than 20 with less than 4 carbons) which could conceivably occur in retort gas, and because of the lack of previous knowledge ragarding the species present, several columns were investigated with regard to their separation ability. These included a acetone-washed Porapak QS, Chromosil 310, Chromosil 330, Carbopack B HT 100 and Carbopack B/1.5% XE 50 + 1% $H_3PO_4$, and an OV-210 treated Porapak QS. An SP-2 100 capillary column was also considered intitially but was discontinued due to its cryogenic requirements and its inability to separate $H_2S$ and COS.

In summary, the ideal column for analyzing retort gas must possess these characteristics:

- Separation of all possible S species (which could in theory number over 20)
- Separation of S species from $C_1$, -$C_4$ hydrocarbons
- Resistance to water vapor and other components in retort gas
- Reproducibility
- Complete an analysis in 30 minutes or less for the rapid testing of control equipment

A simple protocol was developed using a packed column for $H_2S$, COS, $CH_3SH$, $CH_3CH_2SH$, and $CS_2$. $SO_2$ can also be measured depending on the relative size of the neighboring peaks and operations. While capillary columns thus appear promising for future work, they were not persued in depth at this time. It was soon obvious that no packed column could satisfy all criteria, although through use of a selection of columns, several species can be adequately separated, albeit in separate runs.

EXPERIMENTAL

Reagents

Several columns, each six feet long, were packed in 1/8" OD teflon tubing (Supelco, Bellefonte, PA) and tested. Column packings tested were Porapak QS (Waters Associates), OV-210 (Pierce Chemical Co., Rockford, Ill.) on Porapak QS; Carbopack B HT 100 and Carbopack B/1.5% XE 60/1% $H_3PO_4$, both from Supelco (Bellefonte, PA); and Chromosil 310 and Chromosil 330, both of which are treated silica gel packings from Supelco.

Gases were purchased either from Linde Specialty Gases or from Matheson (Joliet, Ill.). The flame photometric detector was operated with "zero" grade gases from Matheson. Two hydrocarbon mixtures containing $C_1$ to $C_6$ alkanes and

$C_2$ to $C_6$ n-alkenes were obtained from Scott specialty gases (Plumsteadville, PA). Liquid mercaptans and thiophenes were obtained from Eastman Organic Chemicals (Rochester, NY). Reagent grade acetone was purchased from VWR Scientific (Denver, CO).

Column Packing Process

Each column was prepared in a six feet length except the acetone-washed Porapak QS, which was prepared in an 18 inch length. A plug of silanized glass wool was placed in one end, which was attached to a vacuum source. The column support was poured into the tubing and compacted with the aid of a vibrator. All materials were used as received from the manufacturer with the exception of Porapak QS, which was first acetone washed, and the Chromosils, which were purchased prepacked.

Notes on the Individual Column Materials Follow--

Porapak QS. Acetone-washed Porapak QS was prepared according to the procedure described by De Souza et al. (1975). 5.0 g of Porapak QS was placed in a Buchner funnel on a piece of filter paper. The Porapak was then washed with 50 ml of reagent grade acetone and allowed to stand for five minutes. A vacuum was then applied for 20 minutes to dry the packing. The column was then packed and then conditioned overnight at 240°C with a carrier flow rate of 55 ml $min^{-1}$.

Chromosil 310 and Chromosil 330. These column materials can be obtained only as pre-packed columns from Supelco. They were selected because of their ability to elute COS before $H_2S$, a feature which is advantageous when trying to determine COS in a large excess of $H_2S$, the situation expected in retort gas. It is also recommended because of its ability to separate higher molecular weight sulfur species (Supelco Bulletin 722G). This column was conditioned at 70°C under a flow rate of carrier gas (He) of 20 ml/min.

Porapak QS/OV 210. This column was prepared by coating acetone-washed Porapak QS, prepared as described above, with OV 210, a trifluoropropyl methyl silicone. To 5.0 g of acetone-washed Porapak QS was added 5 ml of 0.1% v/v OV 210 in reagent grade acetone. The support was coated by swirling the beaker until the acetone evaporated. If the packing was stirred, it tended to break apart, so this procedure was avoided. When the support was dry, the column was packed and then conditioned at 25°C with a carrier flow rate of 40 ml/min for 8 hours.

Carbopack B HT 100 and Carbopack B/1.5% XE 50/1.0% $H_3PO_4$. These columns are graphitic solids supplied by Supelco for the separation of sulfur compounds, especially $H_2S$, $SO_2$, COS, and $CH_3SH$. In addition, the acidified column is optimized for the separation of the isomers dimethyl sulfide and ethyl mercaptan. Since the properties of these two columns were not sufficiently different, and since the acidic column is more difficult to prepare, the latter was not investigated in detail. The Carbopack B HT 100 column was prepared in a manner similar to the other columns. However, because of its fragility the column was not vibrated during the filling process, but was agitated gently by tapping the side with a spatula.

Equipment

Two separate gas chromatography systems were used during this investigation. The first consisted of a Hewlett Packard model 5830A gas chromatograph equipped with a model 18850A integrating terminal, a thermal conductivity detector, and a Varian Associates (Sunnyvale, CA) dual flame FPD which had been specially adapted to the Hewlett Packard gas chromatograph. The second system consisted of a Baseline Industries (Lyons, CO) model 1030A gas chromatograph equipped with a Meloy, single flame FPD (CMS, Austin). This instrument was modified to permit the FPD signal to be recorded by an external

integrator. This FPD is the mechanical design sold by most vendors in this country, although many manufacturers supply their own electronics. The valving and column arrangement of the Baseline System was designed to permit backflushing two columns to the detector without extinguishing the flame and is described in the "Protocol" section of this report. The Hewlett Packard system was configured similarly except that only one column was installed.

Retention times were measured with the Hewlett Packard system using the thermal conductivity detector. This permitted the simultaneous determination of the system dead volume which was helpful in presenting the data in a coherent manner. The quenching effects of the single flame detector were determined by monitoring the Meloy detector with the Hewlett Packard Model 18850A integrating terminal; the response of the dual flame detector was determined using the Hewlett Packard gas chromatograph and integrating terminal. Retort gas samples were analyzed using only the Baseline system in conjunction with a Hewlett Packard model 3390 peak integrator.

Preparation of Gas Standards

All quantitative standards were prepared by blending continuously flowing gas streams. Most such standards were prepared by blending pure gases or gas mixtures with mass flow meters manufactured by Tylan Corp. (Carson, CA). Hydrocarbon components of the gas mixtures were introduced with Matheson model 7642T rotameters. Both rotameters and mass flow meters were calibrated for each gas with dry test meters and bubble meters, both of which were calibrated in reference to NBS standards. Qualitative mixtures (e.g. for the determination of retention times) were frequently prepared in static systems such as teflon bags and glass gas bulbs which had been equipped with teflon-lined septa. The latter was especially convenient for the preparation of qualitive standards of the sulfur species which are normally liquid at room temperature

(such as thiophene). In such cases a few microliters of pure liquid was simply injected into the bulb with gentle heating if necessary.

Procedure for Measuring Signal Quenching

Two different approaches were used for measuring the quenching of the fluorescent signal by co-eluting hydrocarbons. In the first approach calibration curves were obtained for $H_2S$ by varying the amount of $H_2S$ while keeping the concentration of ethane at a constant level of 20% v/v. In the second approach the concentration of $H_2S$ was kept constant at a level corresponding roughly to the middle of the FPD range (~5 ng) while the concentration of ethane was varied. Identical experiments were conducted for methyl mercaptan in the presence of varying amounts of n-butane. All suppression experiments were conducted using an acetone-washed Porapak QS column, six feet long by 1/8 inch od operated at 70°C. The flow rate was set at 30 ml/min for all experiments and the injection volume was 100 µl. This column was selected for the suppression studies because of the naturally occurring peak overlap of ethane with $H_2S$ and methyl mercaptan with butane (see below). However, to further enhance the overlap of the sulfur gas and hydrocarbon, measurements were made during the backflush mode of the column. That is, the sulfur gas/hydrocarbon mixture was injected and allowed to proceed in the normal forward direction for one minute, at which time the flows were reversed so that the sulfur species and hydrocarbon would co-elute in two minutes. Comparison of the retention volumes obtained under backflush conditions indicated essentially indentical retention times. These experiments thus indicate the approximate signal suppression that would be expected due to exactly overlapping peaks which elute in approximately 2 minutes in the forward direction for the type of columns used in this experiment.

The single flame detector was operated with a flow rate of 180 ml/min of air and 140 ml/min of hydrogen. These flow rates were selected by varying the flows of both gases until a plateau was reached in the sensitivity of the response. This detector temperature was set to 140°C, although there was no way of confirming its actual temperature. The single flame detector was operated in two different modes. In the first mode the hydrogen mixed with the carrier gas was introduced concentric and interior to the flow of air. This is how the detector is operated in most cases, and will be referred to as the "normal" mode in this text. In the other mode, referred to here as the "reverse" mode, the air was introduced interior and concentric to the flow of hydrogen.

The dual flame detector requires two air flows and one hydrogen flow to maintain the two flames. Gas flows were as follows: Hydrogen: 140 ml/min; air 2 (to the first flame), 80 ml/min; and air 1 (to the fluorescent flame), 170 ml/min. The temperature of this detector was set to 155°C.

Procedure for Measuring Retention Times

The retention times of each gas were found by injecting one ml of approximately 1,000 ppmv gas and monitoring the response with a thermal conductivity detector. (Lower concentrations were required for the less volatile gases such as thiophene.) Column temperatures were varied to permit elution of the gas of interest in a reasonable time. The carrier gas flow rate was constant at 30 ml/min.

Procedure for Measuring Actual Retort Gas

Samples of actual retort gas were obtained from the pilot scale oil shale retorts located at the North Site of the Laramie Energy Technology Center (DOE). These included the low void volume retort and the 150 ton retort at this site. During routine monitoring the gas was cooled by passage through a

condenser kept in an ice bath to remove excessive water. Selected samples, however, were analyzed from warmer sections of the process without pretreating or cooling the gas for testing the tolerance of the column to the myriad materials and water vapor expected in retort gas.

## RESULTS AND DISCUSSION

### Flame Stability

One of the supposed problems with the FPD is that the flame is easily extinguished by the elution of combustible gases, such as solvents. This occurs because the flame operates with approximately 100% excess hydrogen over that required for stoichiometric combustion and is thus easily extinguished by additional fuel. An initial major concern was the stability of the flame in the detector upon the elution of combustible components in retort gas. This concern proved groundless as the flame once lit, proved entirely stable during the analysis of retort gas once it was lit. However, other aspects of flame stability proved of more concern.

Because the composition of retort gas was likely to include a number of heavier components, including sulfur species, the gas chromatographs were plumbed to permit the column to be backflushed to the detector. With this arrangement it was hoped to estimate the sulfur species not analyzed in forward mode and to preserve the column from degradation during repetitive analyses. However, it was initially observed that the flame would often be extinguished when the backflush valve was activated. This would occur because the flow of carrier gas to the detector would be momentarily disrupted when the valve was between positions; in addition, when the switching was complete, the previously high-pressure end of the column would be on the exhaust end, thereby leading to a sudden burst of gas to the detector. This problem was elimated by installing the flow regulating arrangement shown in Figure 7-1. In this figure the column

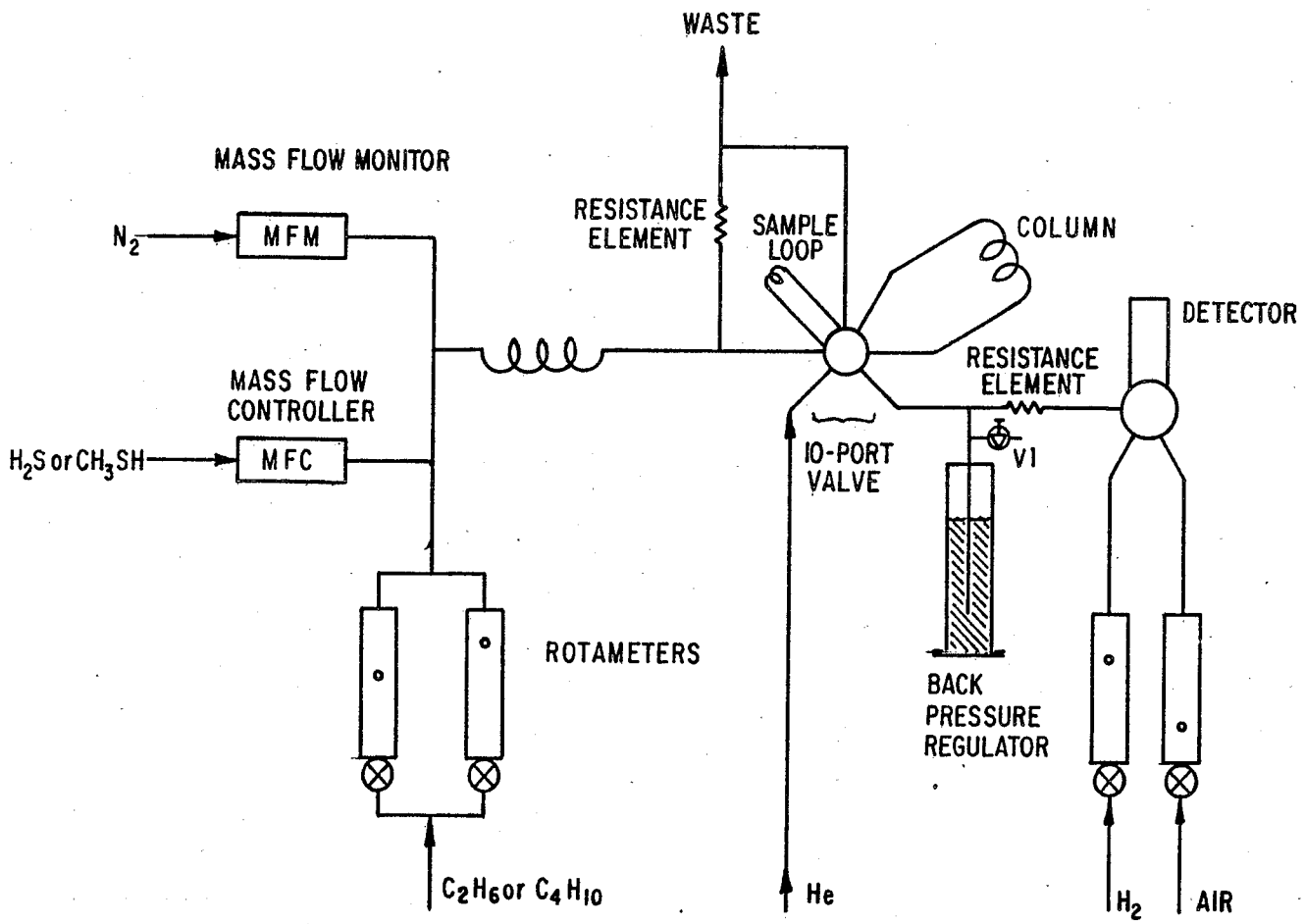


FIGURE 7-1

Column and valve configuration used during the laboratory phase

exhaust does not go directly to the detector, but first passes through a "T" and a resistance element, R. Excess pressure at the "T" is relieved by the back pressure regulator, BPR. In practice the pressure regulator is simply a column of water contained in an acrylic tube into which is submerged a glass tube. The "T" is connected to the glass tube and the height of the tube is adjusted with the carrier gas flowing until the back pressure at the "T" almost, but not quite, causes the gas to escape against the column of water. The resistance element consists of approximately 12 inches of 1/16 inch od stainless steel tubing which is adjusted in length and inside diameter until it causes the required back pressure. Valve V1 in the figure is adjusted to approximately 2 ml/min and is included to avoid the accumulation of sulfur species in that portion of the system. In practice, when the backflush valve is actuated, the column of carrier gas contained in the glass tube first flows backwards to compensate for the interrupted flow, and then bubbles to vent the excess gas corresponding to the previously high pressure end of the column. When operating this system for a period of several days it is necessary to monitor the height of the carrier gas column in the back pressure regulator, since the resistance of the element R apparently changes slowly over time, and carrier gas escaping from the BPR would obviously change the calibration of the system.

The flow regulating system shown in Figure 7-1 has been used during the routine analysis of retort gas samples over a period of several days. During this time the flame was not extinguished during valve actuation, nor during the elution of the sample components. In this sense the flame can be said to be stable during the routine analyses of retort gas.

However, the ease with which the flame could be lit varied markedly with the type of detector and whether the single flame detector was used in the

normal or reverse mode. The single flame FPD, referred to hereafter as the SFPD, could normally be lit on the first attempt when used in the normal mode, although a certain amount of trial and error was required to arrive at a reliable procedure. This procedure consisted of setting the air and the carrier gases to their usual levels with no hydrogen flow. The hydrogen was slowly introduced while the ignition button was depressed, activating a hot filament in the vicinity of the burner head. As the hydrogen flow was gradually increased with the ignition on, the flame would eventually ignite, as evidenced by the appearance of steam in the exhaust from the detector or the deflection of the strip chart recorder. The ignition was maintained while increasing the hydrogen flow until a self-sustaining flame could be obtained, usually in the range of 50 to 80% of full flow. The hydrogen flow was then slowly increased to the correct level. Experience showed that the SFPD in the reverse mode could best be lit in a similar manner, except that the carrier gas was initially turned off, and the hydrogen flow was brought up more slowly and cautiously. After ignition the flame is allowed to stabilize for 5 minutes, after which the He carrier gas is slowly added. In practice the SFPD in the reverse mode was often very difficult to light, and attempts to do so sometimes had to be abandoned. Numerous lighting procedures were attempted, although none proved entirely satisfactory. The authors consider this feature of the SFPD a major impediment to its use in the reverse mode.

In every case the dual flame FPD, referred to hereafter as the DFPD, was very easy to light following the manufacturers instructions: both the air and the carrier gases were set to their final values, and the igniter was activated as the $H_2$ was introduced. The ease of ignition was a definite attractive feature of the DFPD. Although the DFPD was designed, in part, to be less

readily extinguished, it nevertheless required the flow regulation system shown in Figure 7-1 when used in the backflush-to-detector mode.

For each detector the response was less reproducible when the flame was first lit, and a warm-up period of 24 hours was required for best results. This was allowed in every case when quantitative data were required. After such a warm-up period the response to standards was reproducible to 0.5-1.0% relative under laboratory conditions.

Fluorescence Quenching

Figures 7-2 and 7-3 show calibration curves for $H_2S$ obtained on the DFPD as a function of peak area and peak height respectively. The injection volume for each curve is 100 microliters, so that the range of injected $H_2S$ varies from approximately 7-70 ng. Also shown in these figures are the calibration relationships obtained under identical conditions but with the standard containing 20% ethane, corresponding to approximately 2 micrograms per injection.

In both figures no effect due to the added ethane can be observed. For the injection volume employed (100 µl), it can be concluded that 7-70 ng of $H_2S$ (60-600 ppmv) can be determined without interference in the presence of 20 µg (20%) of co-eluting ethane. Since the peak shape is not affected by the injection volume, the same statement applies to the determination of 600-6,000 ppmv of $H_2S$ in pure ethane with a 10 µl sample volume, or to the determination of 6-60 ppmv of $H_2S$ in the presence of 2% ethane with a 1 µl injection volume.

Based on the presumption that other gases behave similarly to ethane and $H_2S$, similar statements can be made for other sulfur species coeluting with other hydrocarbons. Most retort gases contain much less than 20% v/v ethane, and this concentration was chosen as an extreme example. In fact, 2% v/v would

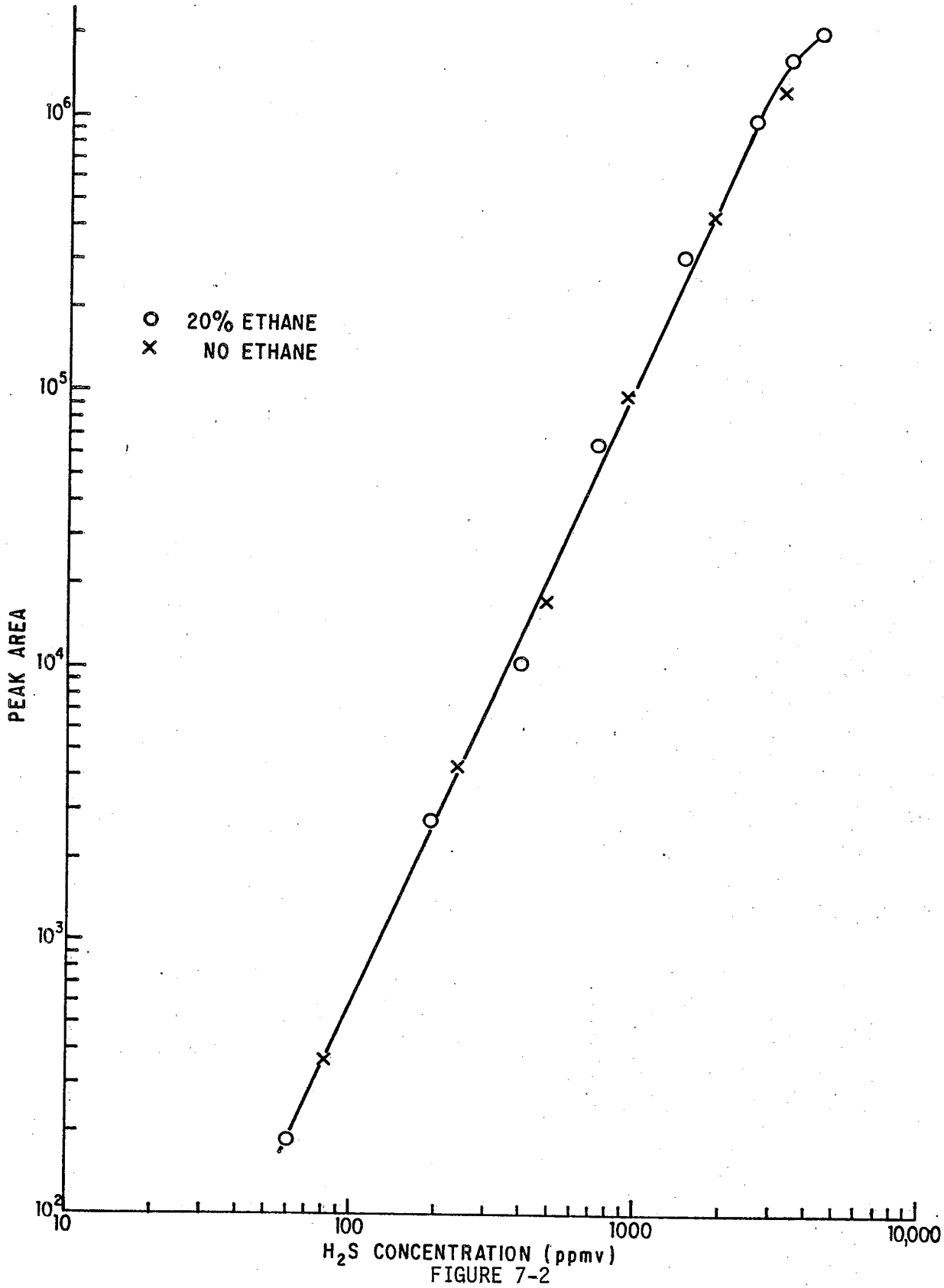


FIGURE 7-2

$H_2S$ calibration curves obtained with the Dual Flame Photometric Detector as a function of peak area

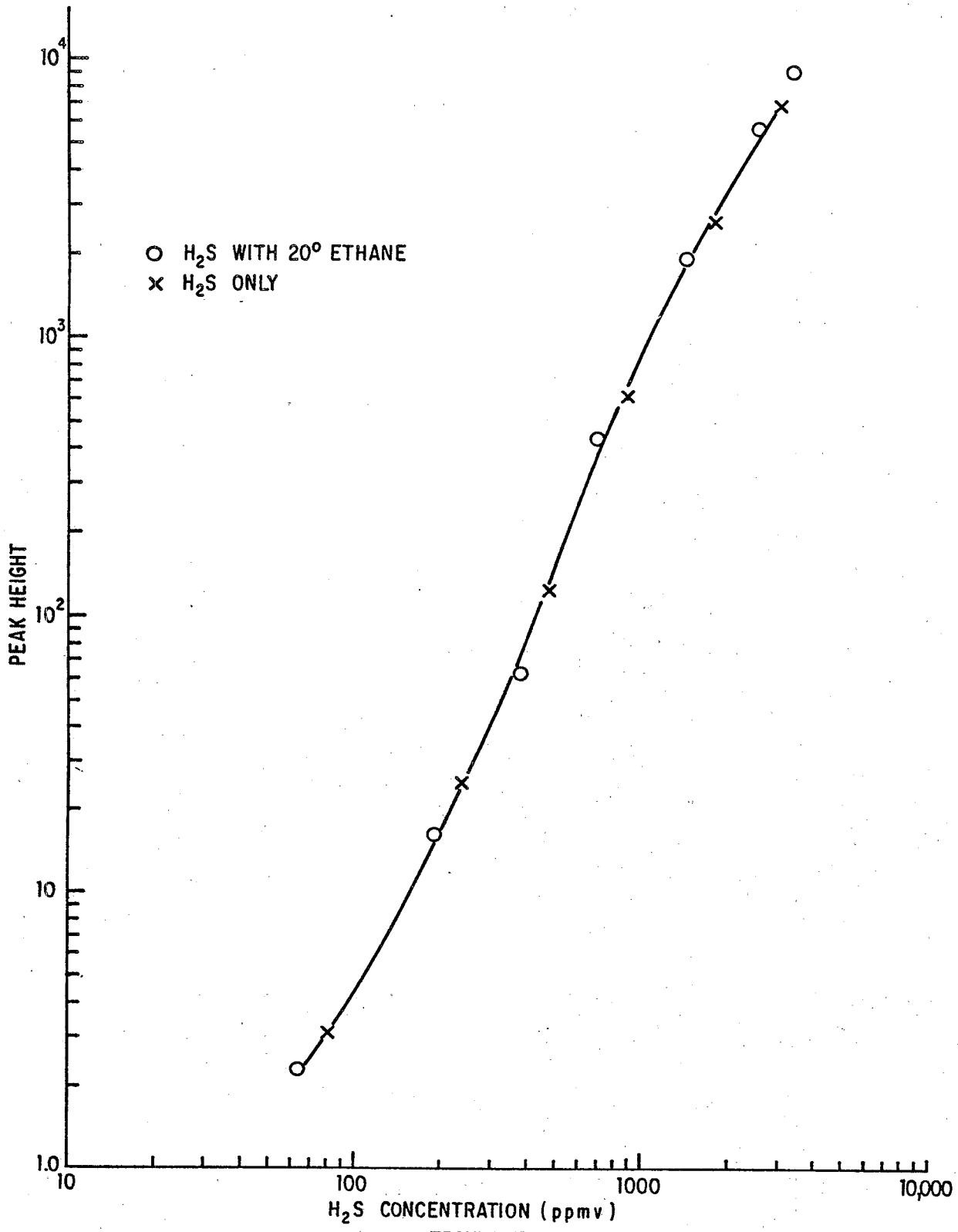


FIGURE 7-3

$H_2S$ calibration curves obtained with the Dual Flame Photometric Detector as a function of peak height

be a more likely upper limit, indicating that the DFPD should be essentially free of quenching effects during the analysis of retort gas.

Figures 7-4 and 7-5 show calibration curves for $H_2S$ obtained on the SFPD operated in the reverse mode as a function of peak area and peak height respectively. The injection volume for each curve was 100 microliters, as for the DFPD. Also shown in these figures are the calibration relationships obtained under identical conditions but with the standard containing 20% ethane, corresponding to approximately 20 micrograms of ethane per injection. Although not clear in this figure, other calibrations of the SFPD have shown its dynamic range, operated under these conditions, to be approximately 1-100 micrograms per injection, somewhat lower than the DFPD.

The effect of the added ethane is clearly visible in either figure, as is the observation that the suppression generally increases with decreasing sulfur content. Referring to Figure 7-4, it is apparent that for a peak area count of 10,000 in the presence of ethane the $H_2S$ concentration would be underestimated by 75% under the chromatographic conditions employed for this experiment. Measurements obtained by peak height would be in error by similar amounts. However, in the peak height mode both signal suppression and enhancement occur in the presence of ethane, a result which, to the authors' knowledge, has not been previously reported in the literature.

Twenty percent ethane exceeds the amount expected in retort gas and such extreme errors would not normally be expected when analyzing actual samples. However, the SFPD is clearly more prone to signal supression by co-eluting hydrocarbons than is the DFPD. Thus, while the DFPD could be used with confidence for essentially any retort gas sample, the SFPD must be applied more cautiously.

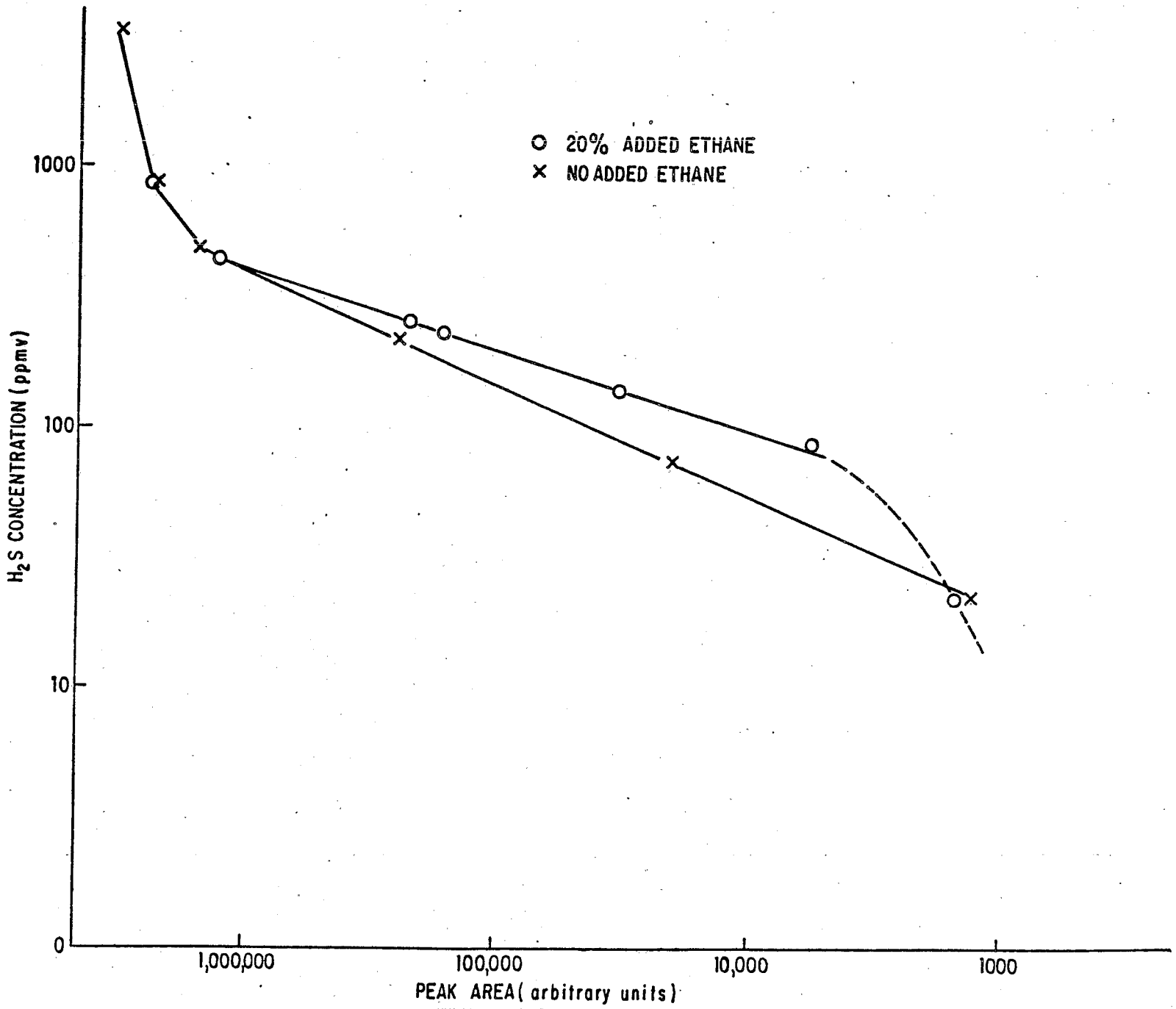


FIGURE 7-4

$H_2S$ calibration curves obtained with the Single Flame Photometric Detector as a function of peak area

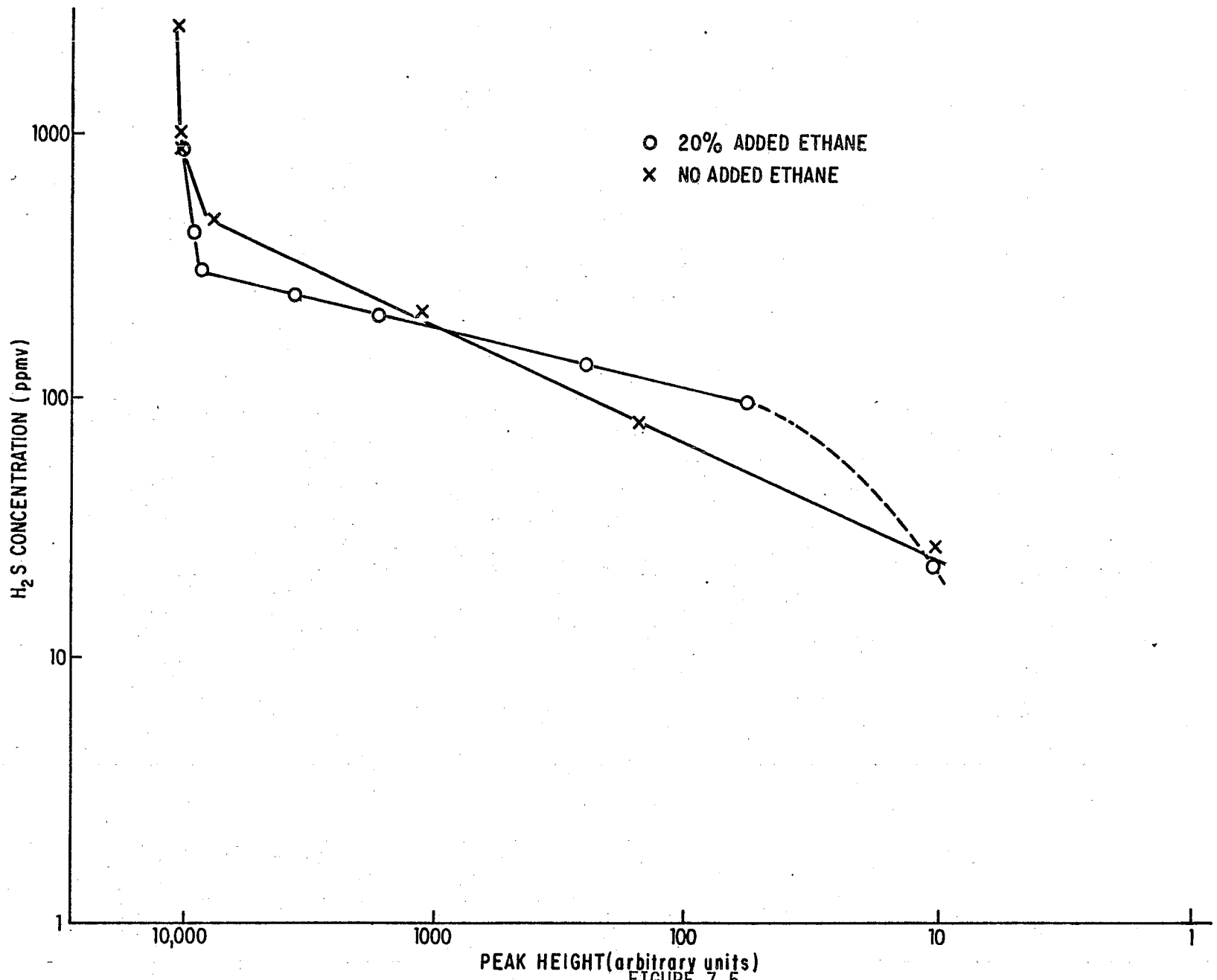


FIGURE 7-5

$H_2S$ calibration curves obtained with the Single Flame Photometric Detector as a function of peak height

Following the same reasoning as applied to the DFPD, one would expect quenching effects similar to those shown in Figures 7-4 and 7-5 if the sample gas contained 2% ethane with a 1 ml sample injection volume, corresponding to a sulfur range of 1-100 ppmv. Slightly less quenching would be expected with a 10 microliter sample injection (100-10,000 ppmv) if the sample consisted of 100% ethane. These results are applicable only to the chromatographic conditions applied in this experiment, consisting of two exactly overlapping peaks eluting from a packed column in approximately 2 minutes. Since the FPD is a flow sensitive detector, similar quenching would be expected under similar flow rates of hydrocarbon and S into the detector. For the experimental conditions discussed, the mass flow rates can be estimated from the peak shape and elution volume. (Based on response of the thermal conductivity detector in this experiment the full peak width at half height was 0.2 min at a flow rate of 30 ml/min.)

Figure 7-5 suggests that the effect of hydrocarbons on the S emission is more complex than a uniform supression of signal, and this is supported by examination of the peak shapes which occur in the presence and absence of hydrocarbons. In the absence of hydrocarbon the $H_2S$ peak is symmetric and normally shaped. Upon the addition of 3% ethane the peak sometimes became slightly higher and often three times narrower. Upon the addition of 60-100% ethane the center of the peak was suppressed more than the edge causing the original S peak to divide into two separate peaks.

The second set of experiments measured signal suppression by injecting a constant mass of S while varying the amount of co-eluting hydrocarbon. Figures 7-6 and 7-7 were obtained with a SFPD operated in the normal and reverse mode, respectively and show the effect of coeluting ethane on the $H_2S$ peak area and height. The indicated points, if taken in the direction of

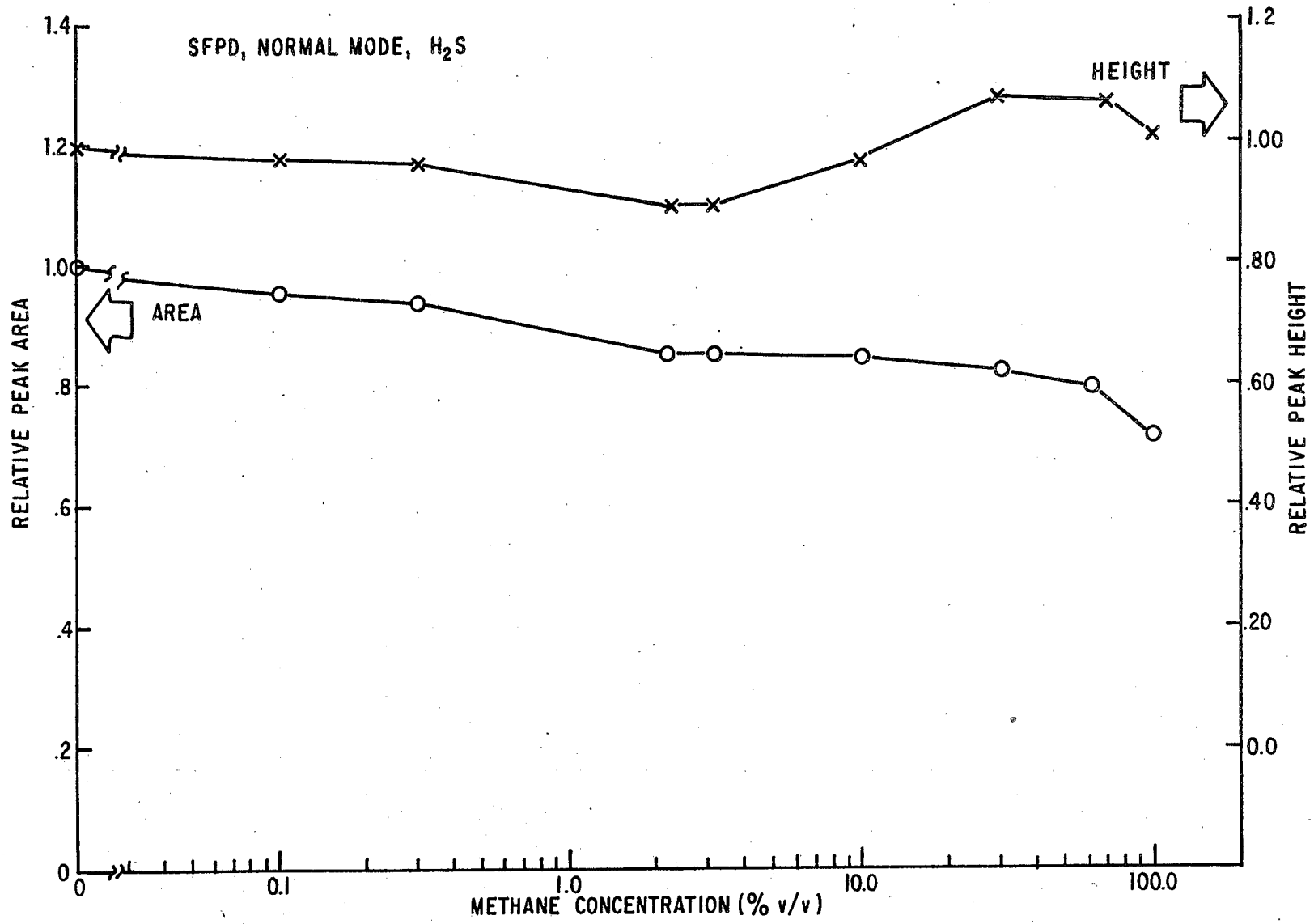


FIGURE 7-6

Quenching of the $H_2S$ signal by co-eluting ethane for the single flame Photometric Detector operated in the normal mode

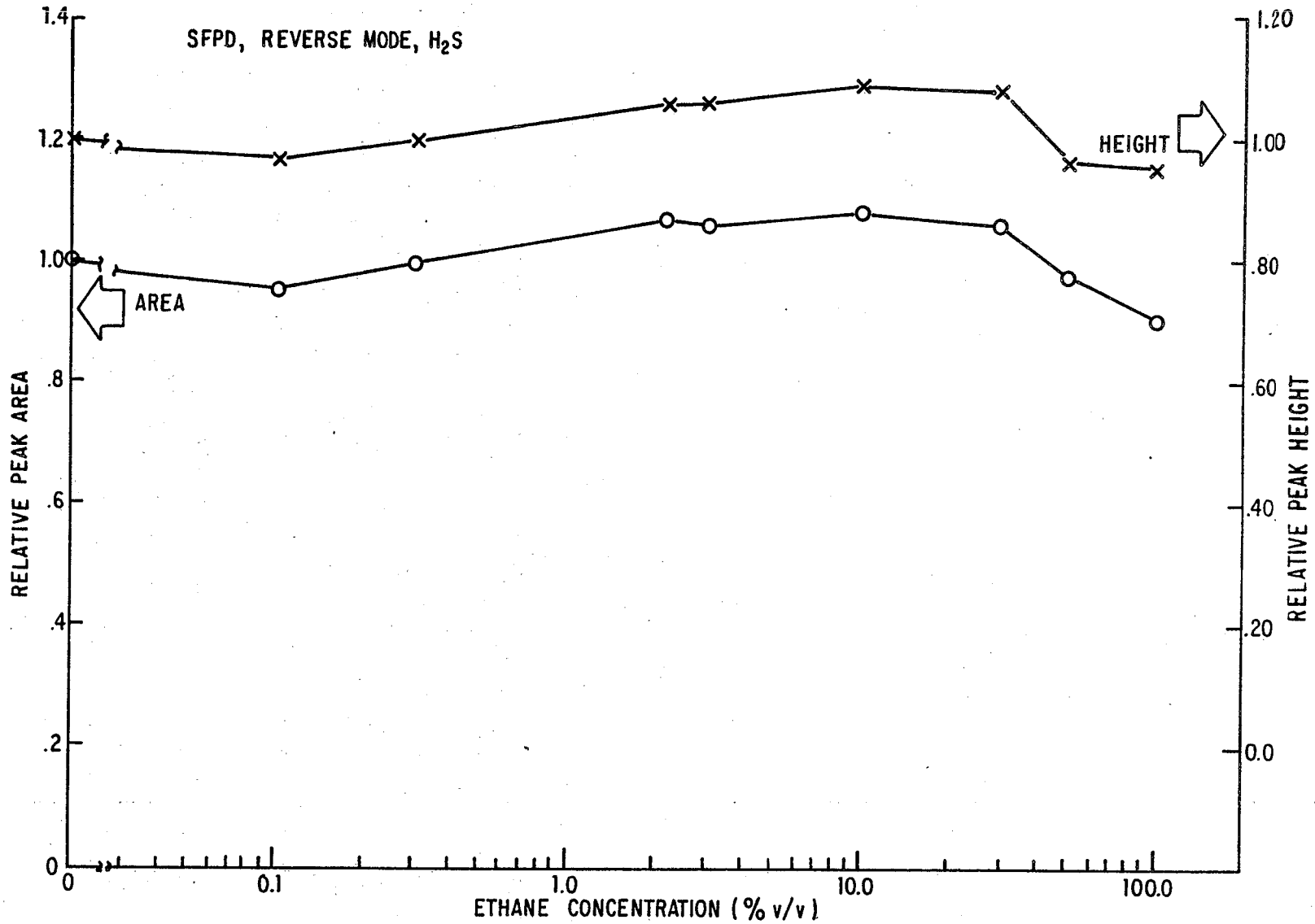


FIGURE 7-7

Quenching of the $H_2S$ signal by co-eluting ethane for the Single Flame Photometric Detector operated in the reverse mode

increasing concentration of added ethane, correspond to 0, 0.1, 0.3, 1.0, 3.0, 10.0, 30.0, and 100.0% added ethane when a 100 microliter injection volume is employed.

The plot of peak area (Figure 7-6) shows a monotonic decrease with added ethane, the so-called fluourescence quenching effect. The remaining three curves are more complex, showing both attenuation and enhancement of the signal. It is difficult to predict from the data in these figures the extent to which fluourescence quenching would be a problem. Of the curves shown, the plot of peak area for the SFPD operated in the normal mode resulted in the largest errors, while the plot of peak height for the SFPD operated in the reverse mode resulted in the smallest errors. For example, for the former plot (peak area, normal mode) an error in the signal of 10% occurs at 1% added ethane, while the latter plot (peak height, reverse mode) does not deviate 10% over the entire range of 1-100% ethane. These data were obtained with a 100 microliter injection volume, and corresponding less quenching would be expected as the injection volume is decreased. Thus, if $H_2S$ were to be measured at a concentration of 5,000 ppmv with a 1 microliter injection volume, the signal quenching would be less than 10% even in pure ethane. Response of the FPD varies with the square of the S concentration, so that a 10% signal suppression leads to a 5% error in concentration.

Experiments identical to those described in the previous paragraphs were performed for methyl mercaptan co-eluting in the presence of n-butane. These data are shown in Figures 7-8 and 7-9 for the SFPD in the normal and reverse mode respectively. These figures illustrate that signal suppression is more pronounced than for the experiments with $H_2S$. For example, for the plot of peak area in the normal mode the signal is attenuated 22% upon the addition of only 0.1% butane. For the plot of peak height obtained from the normal mode,

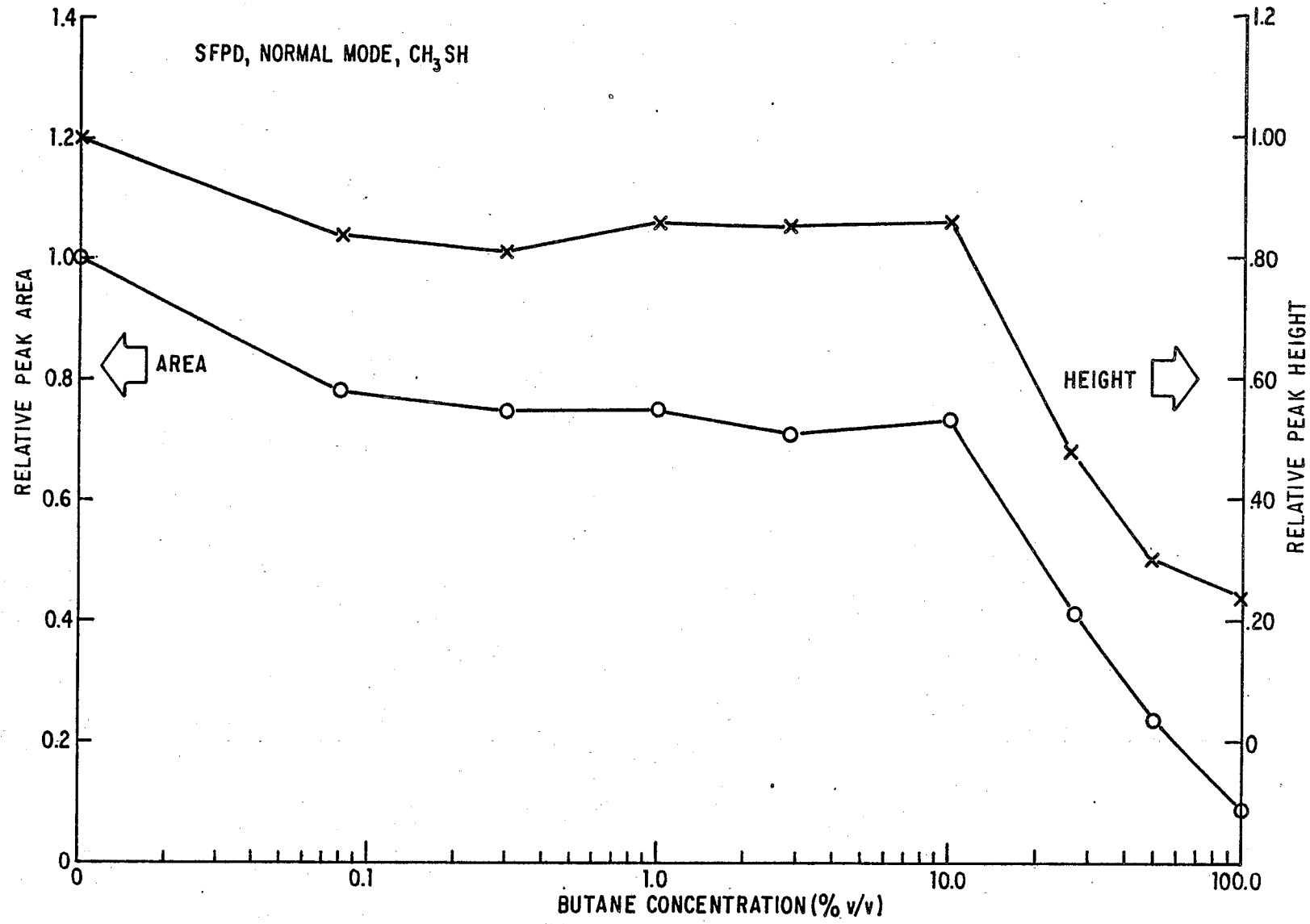


FIGURE 7-8

Quenching of the methyl mercaptan signal by co-cluting butane for the Single Flame Photometric Detector operated in the normal mode

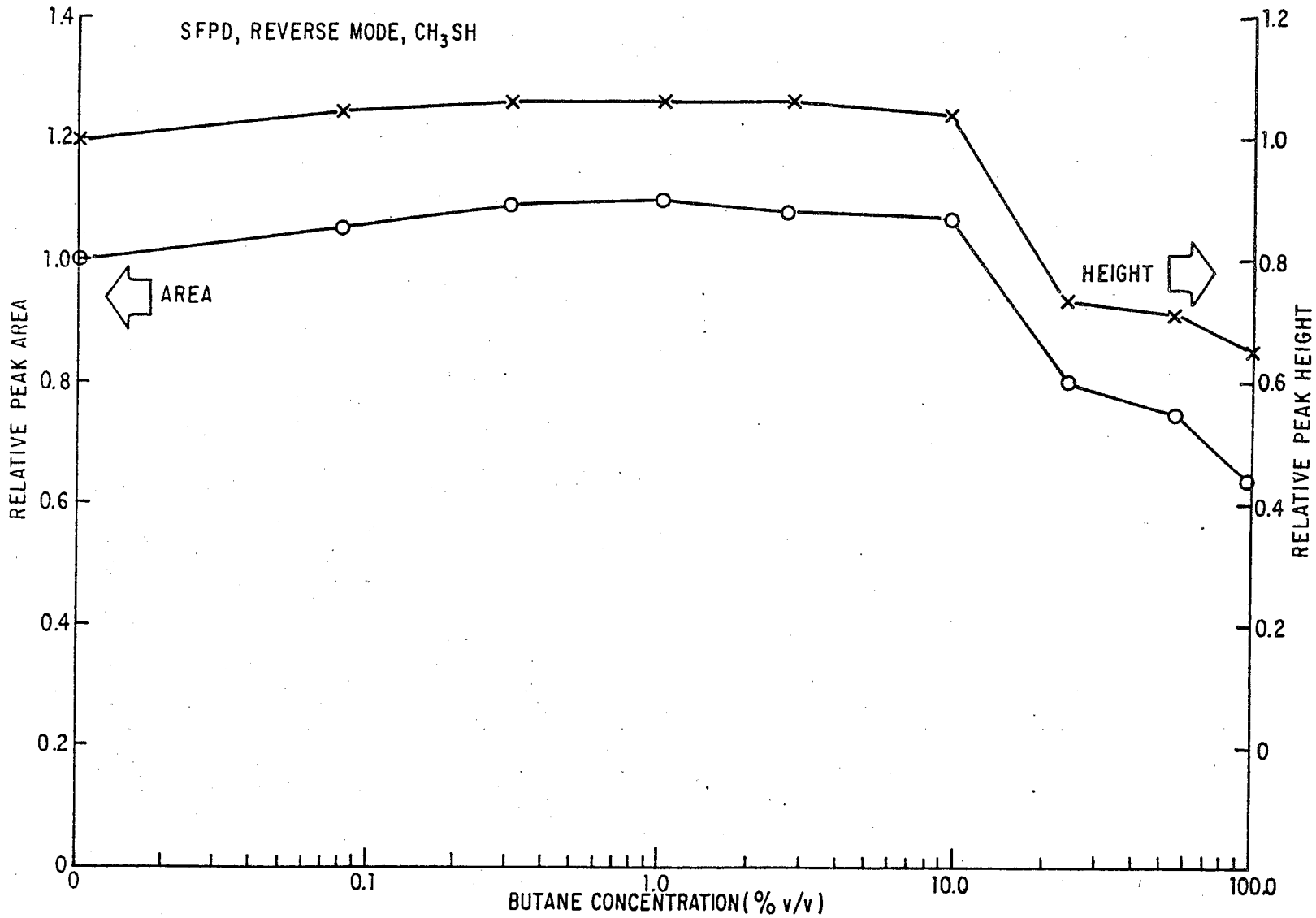


FIGURE 7-9

Quenching of the methyl mercaptan signal by co-eluting butane for the Single Flame Photometric Detector operated in the reverse mode

the addition of 0.1% butane results in an attenuation of 15%. When the detector is operated in the reverse mode, the same addition of butane results in a signal enhancement of 5% in terms of peak area and of 4% in terms of peak height. When the detector is operated in the reverse mode, the peak area is within 10% of the correct value until 0.6% butane is added, but then declines to 90% of the original value upon the addition of 30% butane. Examining the plot of peak height for the reverse mode indicates that the signal is within 6% of the correct value until 20% butane is added. While peak attenuation is observed in all figures, it is apparent that hydrocarbon interference is minimized by operating the SFPD in reverse mode and by using peak height as the calibration parameter.

In relating this data to the analysis of retort gas, recall that an error of 10% in the FPD signal generates a 5% error in concentration. According to these data, then, 95% accuracy could be achieved in the presence of 0.6% butane by measuring peak area in the reverse mode, or in the presence of 20% butane by measuring peak height. These results apply to a 100 microliter sample injection, which corresponds to a concentration range of approximately 10-1,000 ppmv of S, and should be adjusted accordingly for different concentration ranges. Thus, assuming the range of interest for S compounds in retort gas is above 10 ppmv, the data suggest that determinations can be obtained with a 95% accuracy by using the SFPD in the reverse mode and calibrating against peak height.

Identical experiments were carried out with the DFPD, and these results are shown in Figure 7-10 for $H_2S$ in the presence of ethane and in Figure 7-11 for methyl mercaptan in the presence of n-butane. In the case of $H_2S$/ethane attenuation is not observed except at the highest concentrations. The same is true of the methyl mercaptan/butane results. The DFPD all but eliminates the

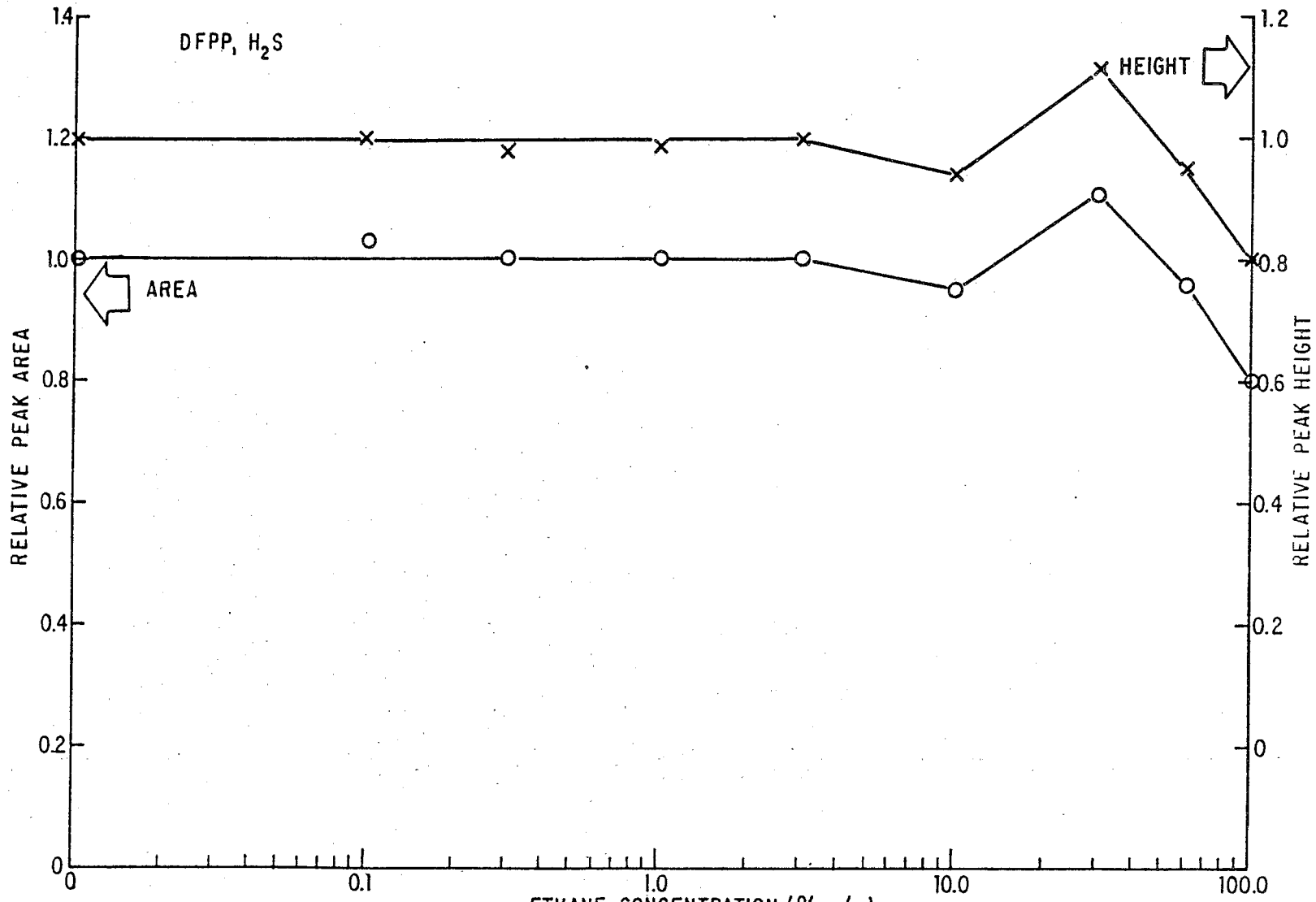


FIGURE 7-10

Quenching of the $H_2S$ signal by co-eluting ethane for the Dual Flame Photometric Detector

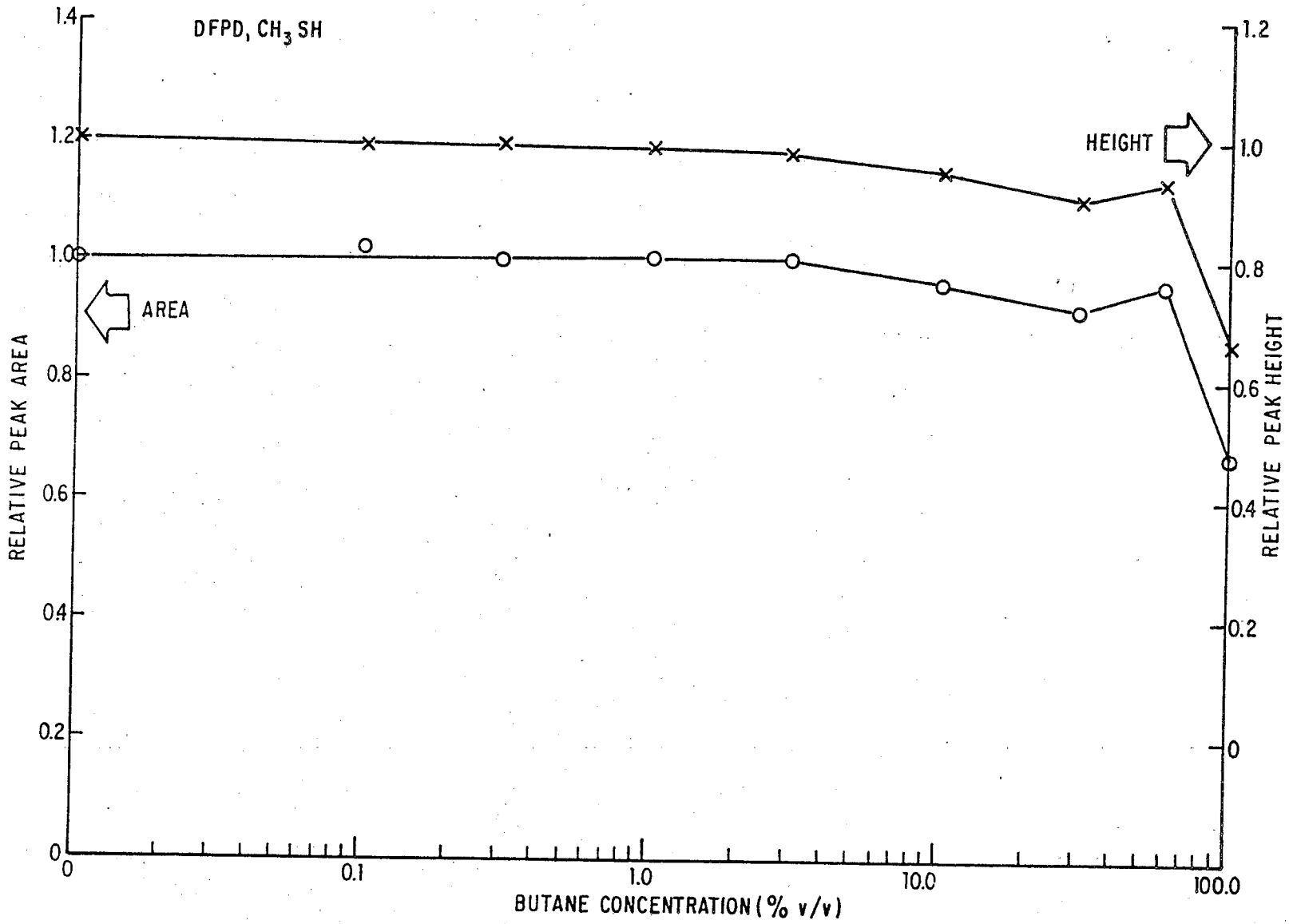


FIGURE 7-11

Quenching of the methyl mercaptan signal by co-eluting butane for the Dual Flame Photometric Detector

interference effect except possibly at concentrations of added hydrocarbons which are greater than would be encountered in retort gas.

Each of these detectors has its limitations. The DFPD appeared to be more sensitive to variations in flow rate of the carrier gas and is more prone to develop light leaks which have the effect of degrading the dynamic range to a point of marginal utility. This requires occasional replacement of light seals. However, the SFPD is more prone to quenching, an effect which is minimized by calibrating with peak height and operating in the reverse mode. However, in the reverse mode the SFPD flame is difficult (sometimes impossible) to ignite.

The mechanism(s) of signal quenching has not been addressed in this report. However, several types of mechanisms have been proposed including (1) interference in the formation mechanism of the activated S species; (2) reaction with the activated S species; (3) absorption of the emitted radiation by hydrocarbon decomposition products; and (4) a change of the position of the H-rich emission region in the flame. Further information is present in the literature (Gilbert, 1970; Patterson et al., 1978).

Uniformity of Response

In theory one could quantitate the various S species by calibrating the FPD separately for each species. In practice, it becomes prohibitive to be prepared to calibrate for every S species, especially in a field laboratory with limited space and facilities. It would obviously be preferable to calibrate with only a few species and then infer from their responses the calibration of the remaining gases.

For this reason the relative responses of four S species--$H_2S$, $SO_2$, $CS_2$, and thiophene, representative of different compound classes, were determined. Standards of these gases were injected in one microliter quantities onto a

Chromosil 310 column at 70°C; detection was by SFPD operated in the normal mode. In this experiment the current from the detector was recorded on a strip chart recorder and entered in digital form with a model 9874A digitizer into a model 9845B desk top microcomputer (Hewlett Packard). The linearized peak area, A', was then calculated according to the expression

(1) $$A' = \int i^{\frac{1}{2}} dt$$

where i = detector current
t = time
k = arbitrary constant

To the extent that the FPD responds to the mass flow of S independent of the molecular form, the quantity A' should be independent of the species which are injected, as well as elution time and peak shape.

Table 7-1 lists the relative responses obtained for these four compounds in terms of linearized peak area per ng of S. Relative responses of these compounds, which represent a disparate group, vary from 1.1 to 5.6. This suggests that relative responses of various S species would fall within a factor of three of an average value, although such a conclusion would require additional testing. Based on the data presented in the previous section, the DFPD or the SFPD operated in the reverse mode would presumably demonstrate less variation in relative responses. However, time and budget did not permit further investigation of this possiblity, and until such testing is performed, it is evident that the FPD of either variety must be calibrated with the gas of interest to obtain quantitative results.

Column Characterization

Retention data for the columns investigated are grouped as follows: the S gases of most interest--$H_2S$, COS, $CS_2$ methyl mercaptan, and $SO_2$--are grouped together and are referred to as the primary S gases. The S gases of less interest--dimethyl sulfide, dimethyl disulfide, ethyl mercaptan, thiophene,

Table 7-1

RELATIVE RESPONSE OF THE FPD TO FOUR SULFUR GASES
WITH THE SINGLE-FLAME FPD OPERATED IN THE NORMAL MODE

| Gas | Concentration (ppmv) | $A' = \int i^{\frac{1}{2}} dt$ (arbitrary units) | A'/mass of S ($ng^{-1}$) |
|---|---|---|---|
| $H_2S$ | 4,927 | 12.5 | 2.68 |
| $SO_2$ | 15,000 | 15.69 | 1.10 |
| $CS_2$ | 5,010 | 53.6 | 5.67 |
| Thiophene | 4,544 | 15.89 | 2.83 |

2-methyl thiophene, 3-methyl thiophene, and t-butyl mercaptan--are also grouped together and will be referred to as the secondary S compounds. The hydrocarbons examined include methane, ethane, ethene, propane, propene, and n-butane; data for these species are also grouped together. Retention time data are also included occasionally for water and ammonia. For each column the adjusted retention time, $t_r$, which is defined as the absolute retention time less the dead volume elution time, is plotted as a function of column temperature. Such plots are normally straight lines over the temperature range of interest for this study, which simplifies data collection and presentation.

To some extent the division of the S species into primary and secondary groups reflects the philosophy behind this effort, which was to develop a simple analytical protocol for the most important S species in retort gas. At the beginning of this project, however, it was not clear which compounds should be considered the most important, although it has long been considered that $H_2S$ is the predominant S species in retort gas. Preliminary reports have also noticed the presence of $CS_2$, methyl mercaptan, and COS in retort gas and other synthetic fuel gases (Sklarew et al., 1981), and these compounds were therefore included in the primary group. Although $SO_2$ has not been reported in retort gas to the authors' knowledge, it was nevertheless of interest due to its common occurrence in combustion gases. The presence of $SO_2$ has also been proposed as a precurser to various S species of intermediate oxidation state which are found in the condensate from retort gas (Stuber et al., 1978). The objective of this work thus became development of a procedure for determining the primary S species in retort gas in a manner which was free from interferences by other S species, that is, free from interferences by the secondary S species and also free from significant quenching by co-eluting hydrocarbons. In final analysis, this division into primary and secondary

groups is somewhat arbitrary, since some secondary S species may eventually be found at higher concentrations than primary S species.

Retention times for the Porapak QS column are shown in Figures 7-12, 7-13 and 7-14 for the primary S species, secondary S species, and hydrocarbons, respectively. Although an adequate separation of the primary S species can be obtained, for example at 90°C, all secondary species elute so closely as to be essentially inseparable. The secondary species elute on top of the primary species COS, $SO_2$, and methyl mercaptan, making this column useless for the analysis of retort gas except for $H_2S$ and possibly $CS_2$. Indeed, the same comment would apply for any type of sample gas except those known not to contain any of the secondary S species. Ethane and ethene both elute essentially simultaneously with $H_2S$, precluding the use of this column for the determination of $H_2S$ in gas streams containing high levels of either of these species. More than one batch of acetone-washed Porapak QS was prepared during this experiment, and it was observed that the retention times varied widely for this column. In addition, although $SO_2$ tailing was not a problem with freshly prepared columns, it tailed for several minutes on columns which had been used for longer periods. On the other hand, one major advantage of this column, which consists of a styrene-divinylbenzene polymer, is its resistance to water vapor, which is often one of the major components of retort gas. Thus, while this column packing appears to be of little use for other species, it may be worthwhile for $H_2S$, as long as the levels of ethane and ethene are sufficiently low. This column was also evaluated during a run of several days using actual retort gas, as discussed below.

Figures 7-15 to 7-17 illustrate the retention times that were obtained with 1% OV 210 on Porapak QS. Among the primary group, $H_2S$, $CS_2$, and methyl mercaptan are well separated, although COS and $SO_2$ are not. The former

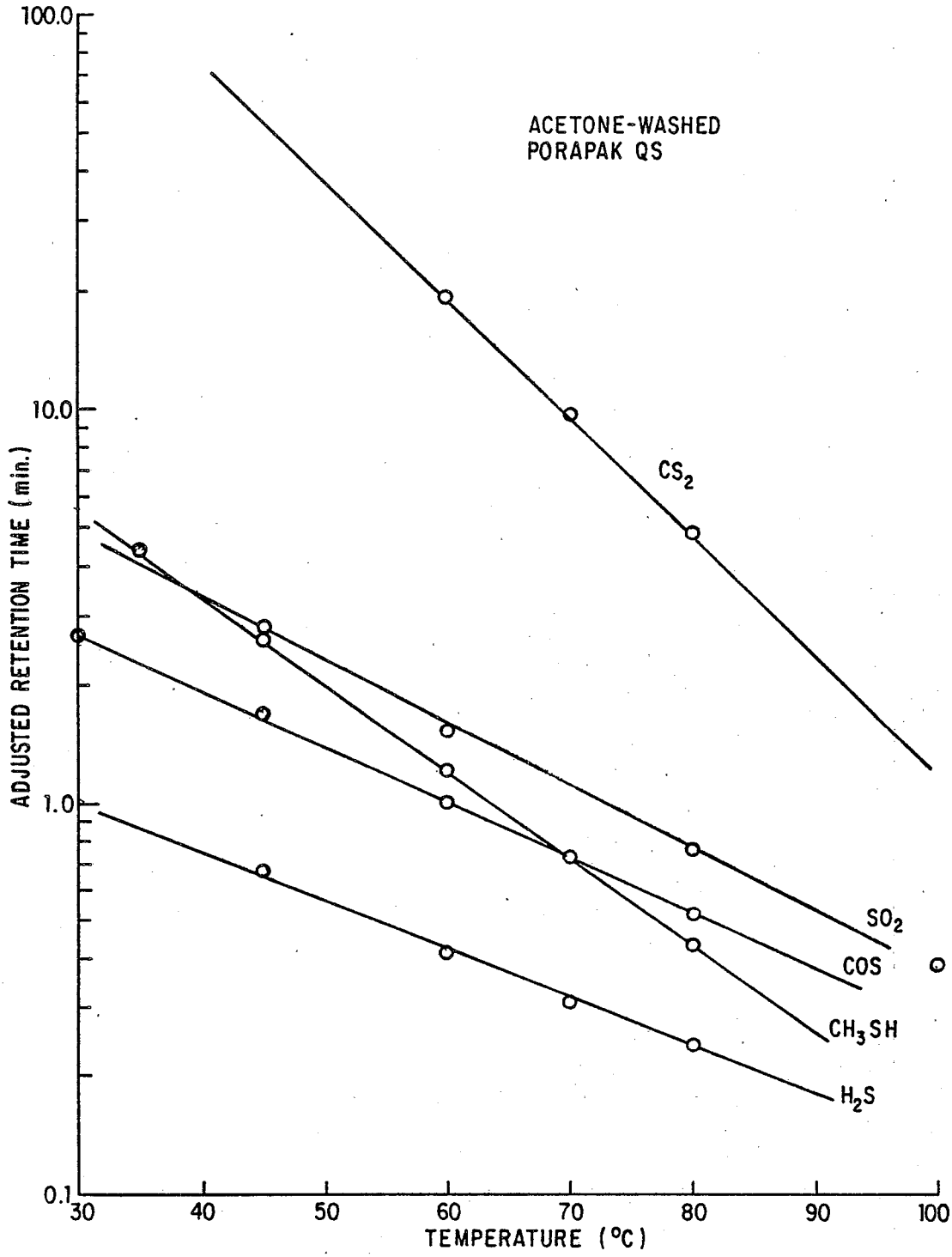


FIGURE 7-12

Retention times for the primary sulfur compounds with acetone-washed Porapak QS

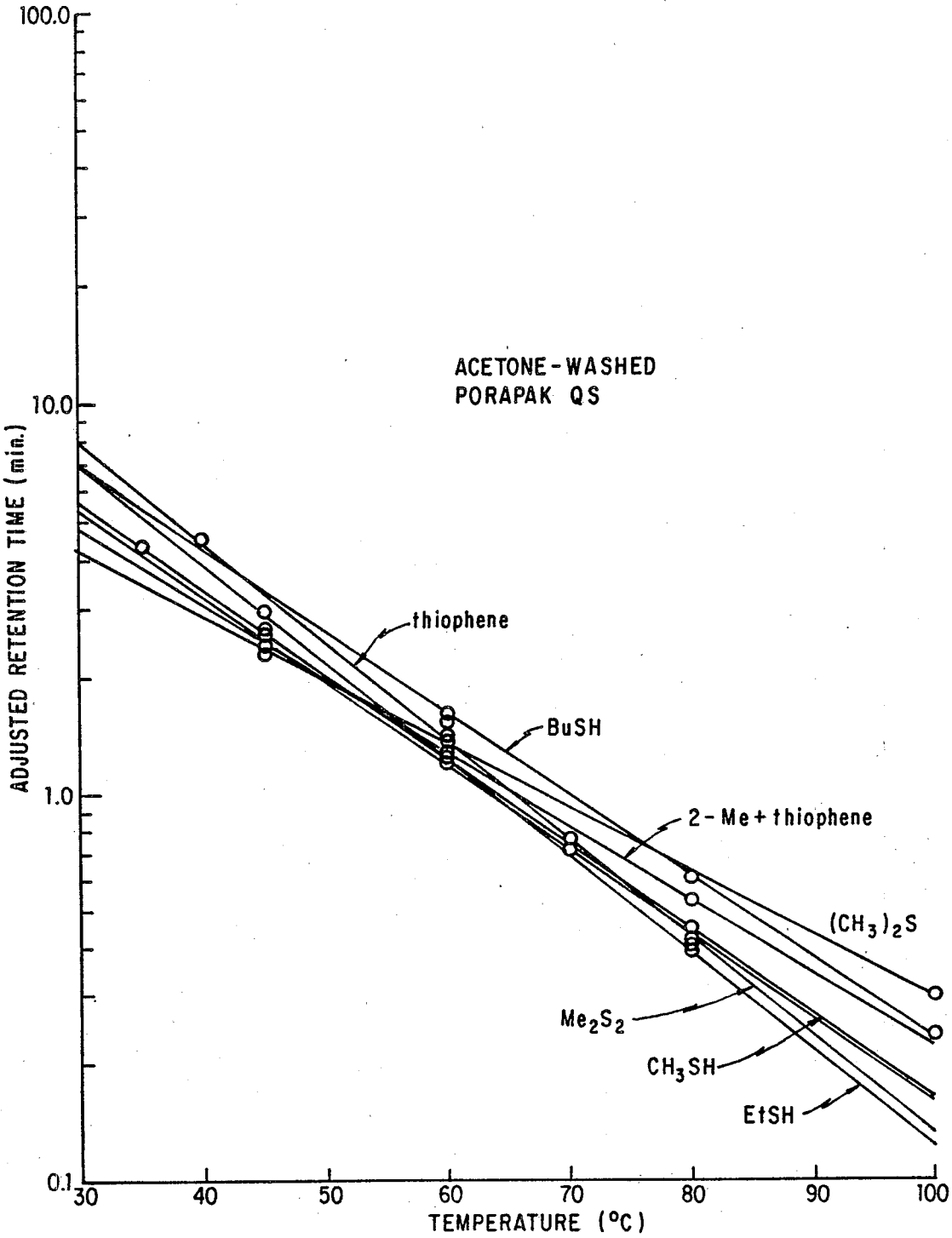


FIGURE 7-13

Retention times for the secondary sulfur compounds with acetone-washed Porapak QS

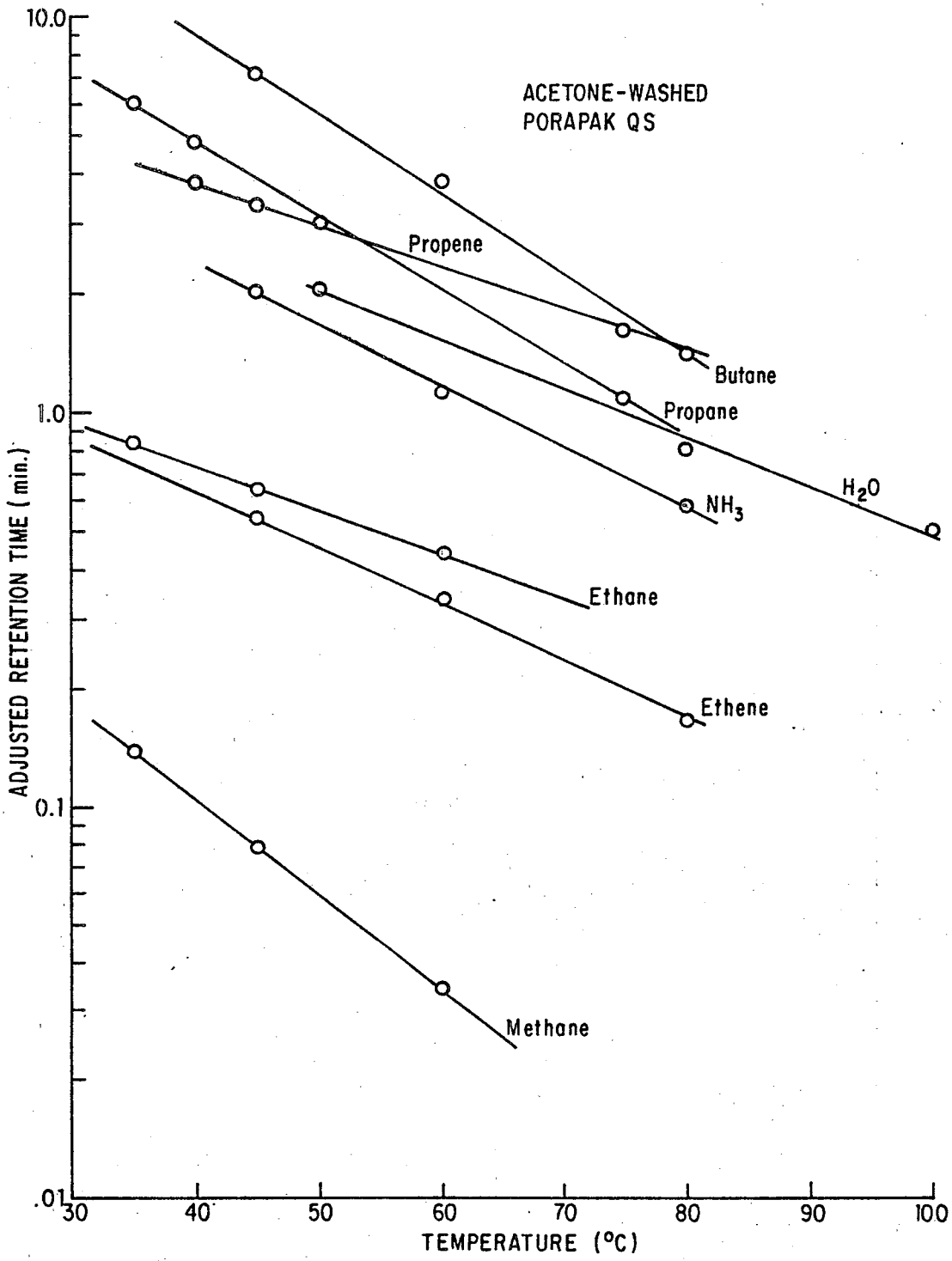


FIGURE 7-14

Retention times for hydrocarbons with the acetone-washed Porapak QS

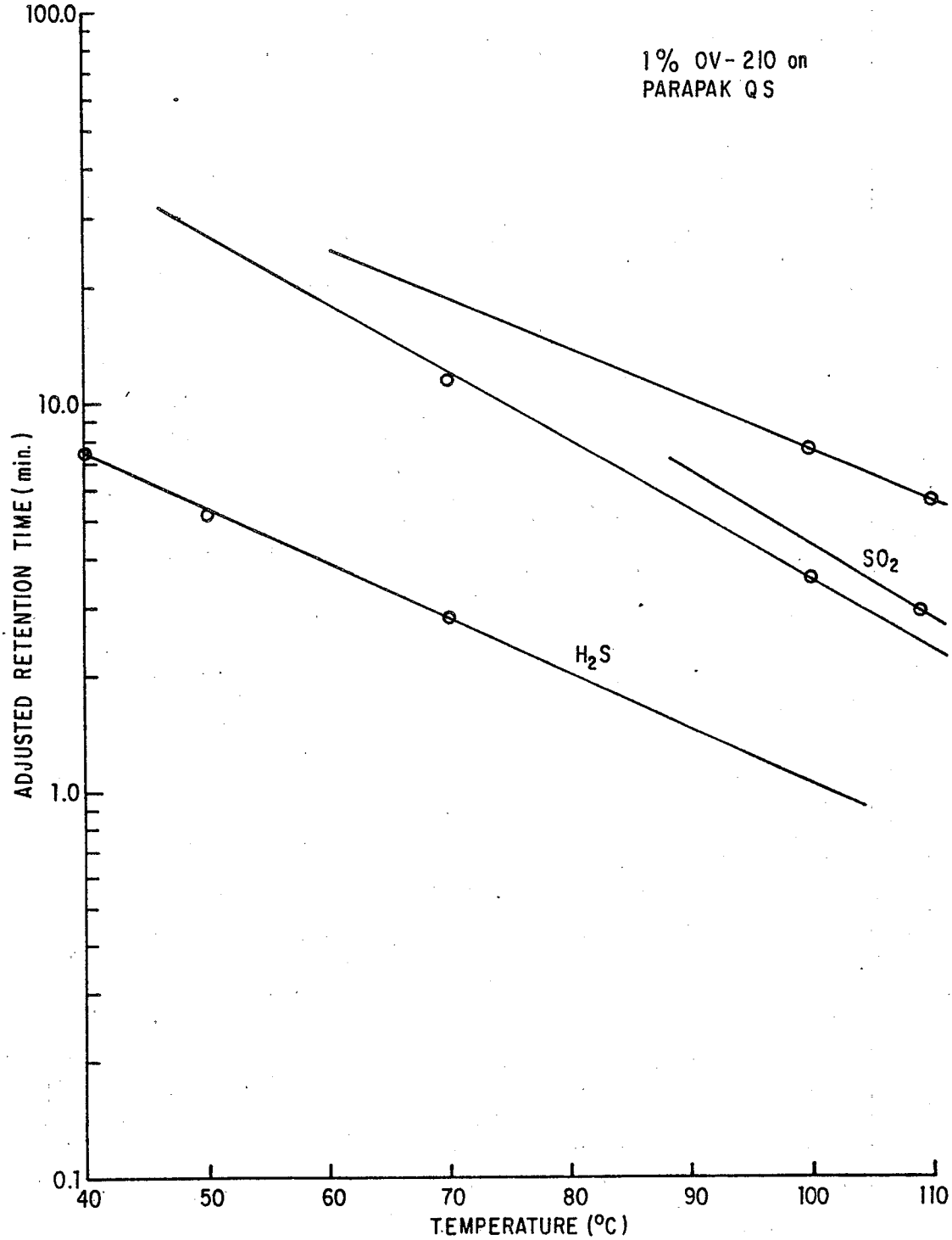


FIGURE 7-15

Retention times for the primary sulfur compounds with OV-210 on Porapak QS

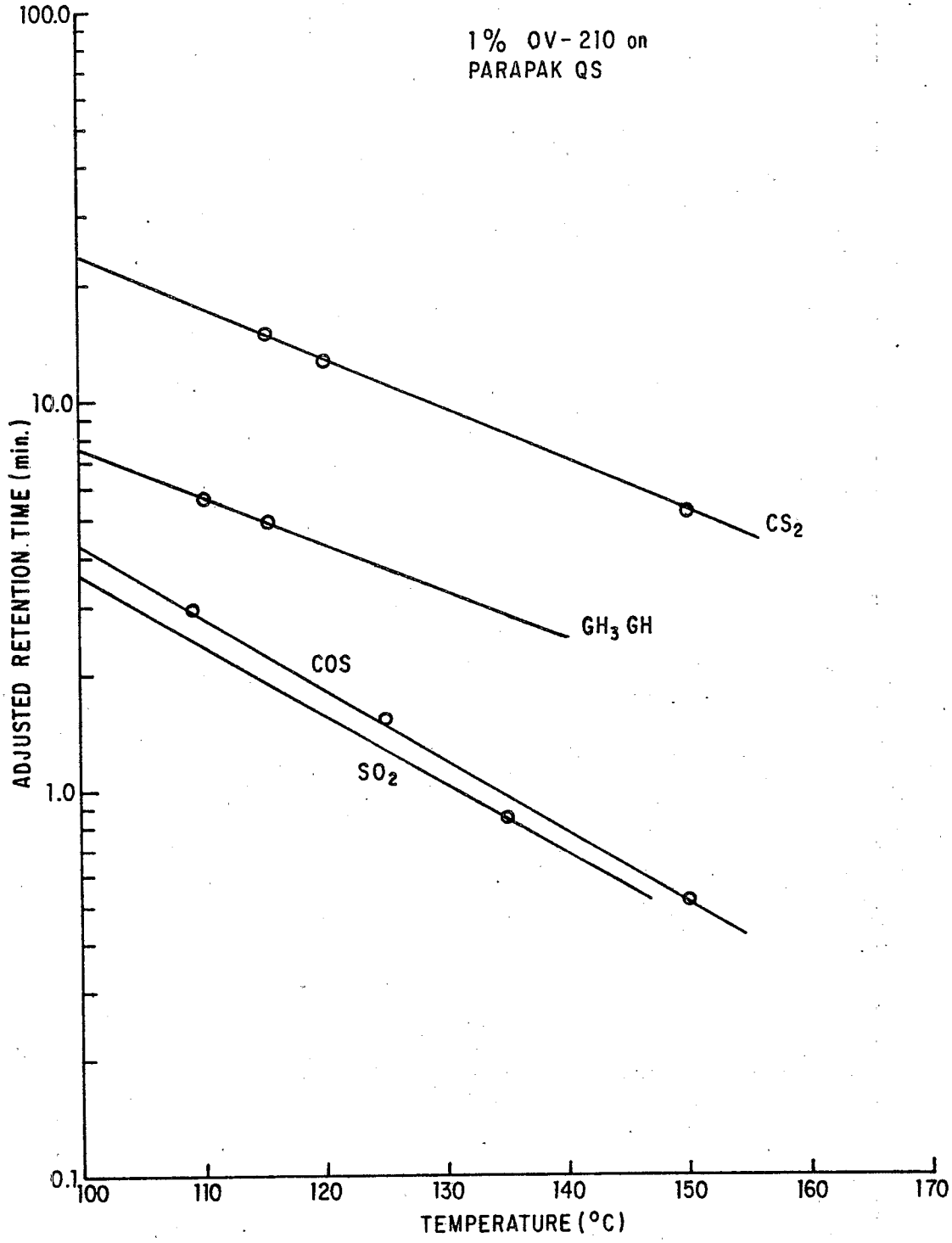
1% OV-210 on
PARAPAK QS
100.0
10.0
1.0
0.1
ADJUSTED RETENTION TIME (min.)
CS2
GH3 GH
COS
SO2
100
110
120
130
140
150
160
170
TEMPERATURE (°C)

FIGURE 7-15(a)

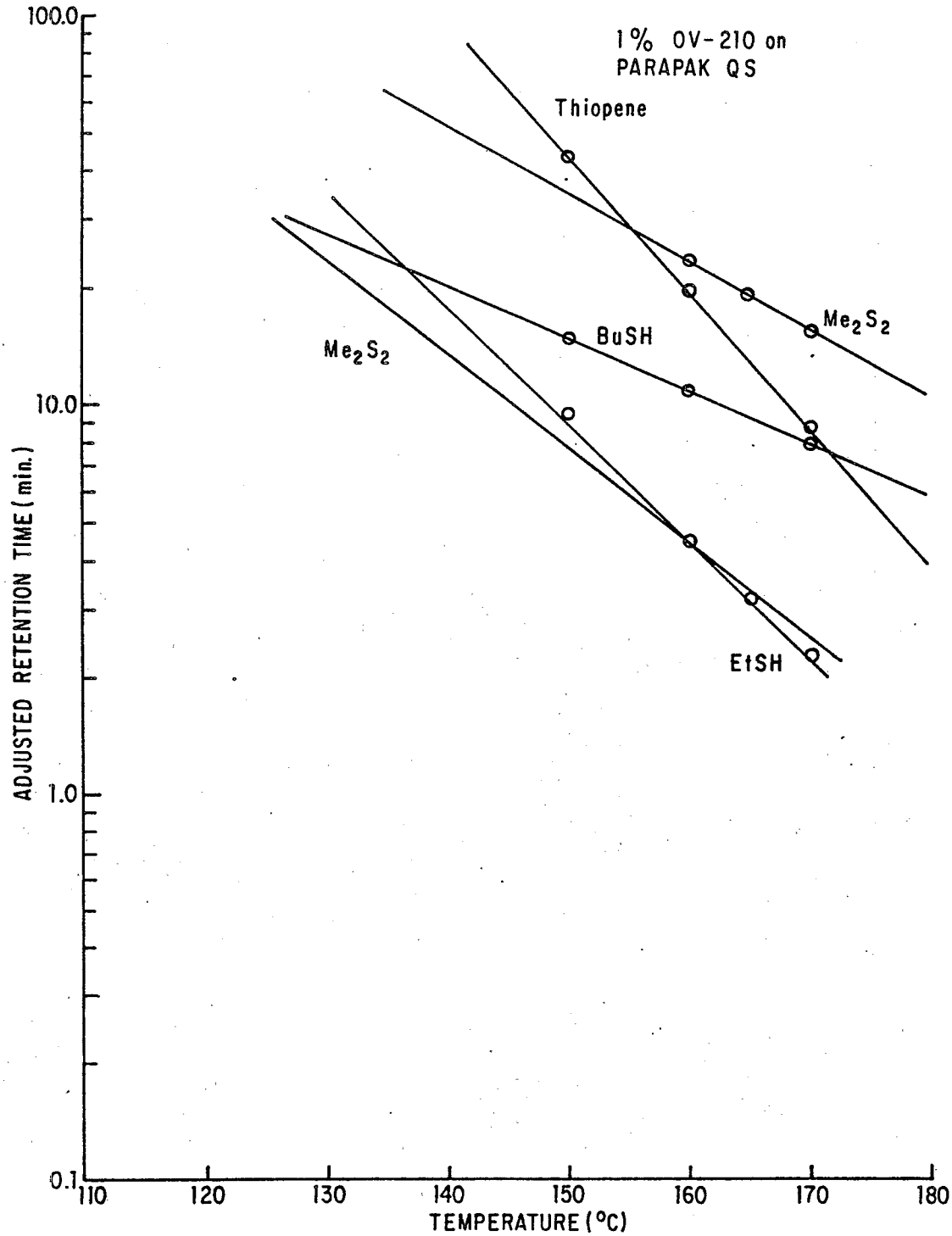


FIGURE 7-16

Retention times for the secondary sulfur compounds with OV-210 on acetone-washed Porapak QS

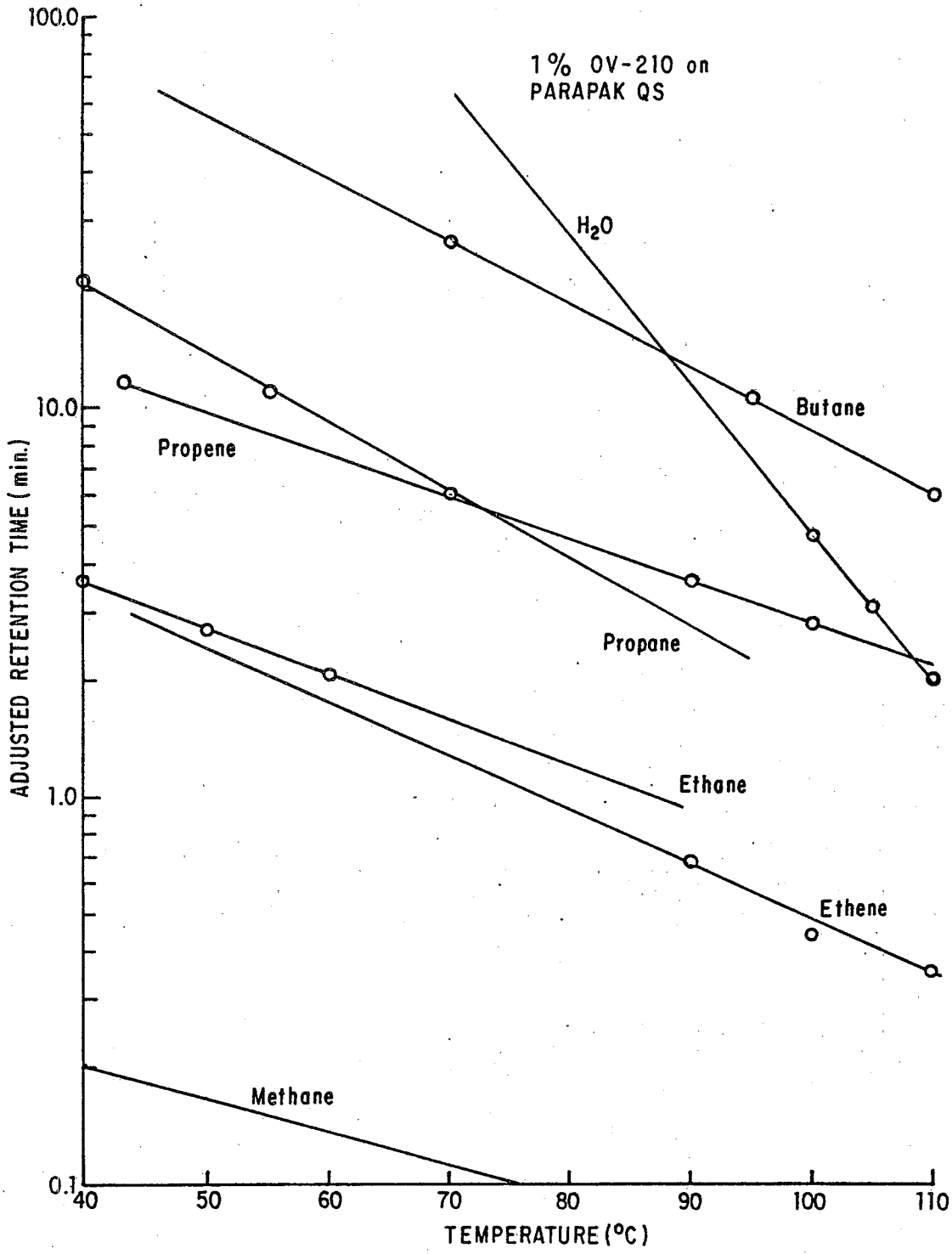


FIGURE 7-17

Retention times for hydrocarbons with OV-210 on acetone-washed Porapak QS

compounds are also well separated from the secondary S compounds, indicating that this column may be useful for $H_2S$, COS, and methyl mercaptan. Preliminary examination of Figure 7-16 suggests that this column may have some utility for the separation of the secondary group. For example, at 165°C the compounds thiophene, n-butyl mercaptan, and dimethyl disulfide are separated. However, the isomers ethyl mercaptan and dimethyl sulfide are not separated, and it is likely that the similar isomer pairs for propyl and butyl mercaptan would similarly co-elute. Further consideration indicates that there are several additional possible S compounds which should elute between ethyl mercaptan and dimethyl disulfide in the figure. These include n-propyl mercaptan, isopropyl mercaptan, the iso- and tert-butyl mercaptans, and the various methyl thiophenes. It thus appears that in order to apply this column to the determination of the secondary S species, one would have to know beforehand which species to expect.

Comparison of Figures 7-15 and 7-17 indicates that $H_2S$ is well separated from the $C_2$ and $C_3$ hydrocarbons. This suggests that for $H_2S$ in high levels of $C_2$ or $C_3$ hydrocarbons, the OV-210/Porapak QS column is preferred over the untreated Porapak QS column.

While this column might be useful for the determination of $H_2S$, it was a difficult column to prepare and stabilize, repeated large injections of $H_2S$ being required for this purpose. Another undesirable feature of this column was that the retention times were too long to permit routine, repetitive analyses every 30 minutes, which was one of the criteria of this analysis. For these reasons as well as its inability to separate COS and $SO_2$, this column was not tested extensively with retort gas.

Figures 7-18 to 7-20 illustrate the retention times obtained with the Chromosil 310 column. Dimethyl disulfide and t-butyl mercaptan are not shown

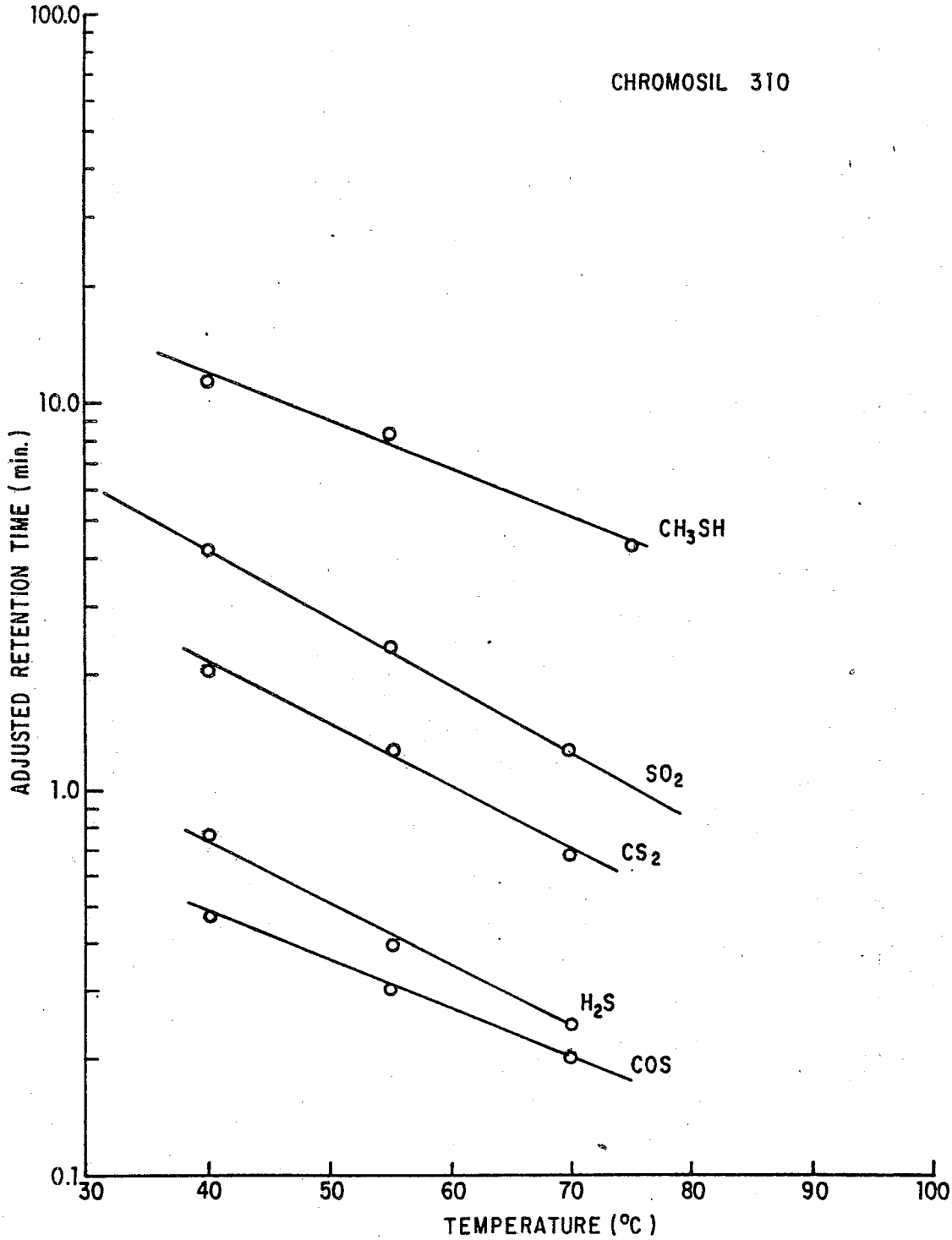


FIGURE 7-18

Retention times for the primary sulfur compounds with Chromosil 310

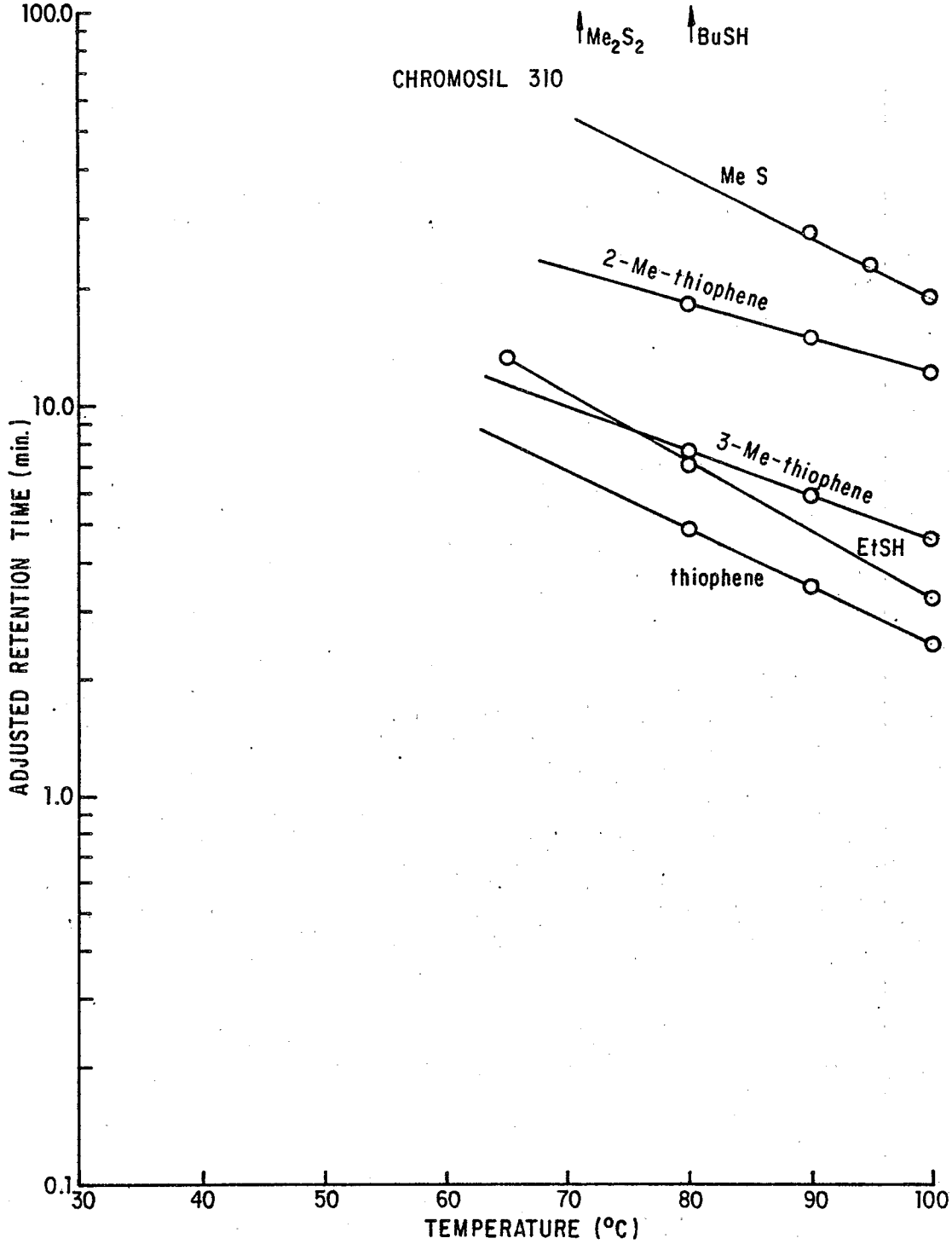


FIGURE 7-19

Retention times for the secondary sulfur compounds with Chromosil 310

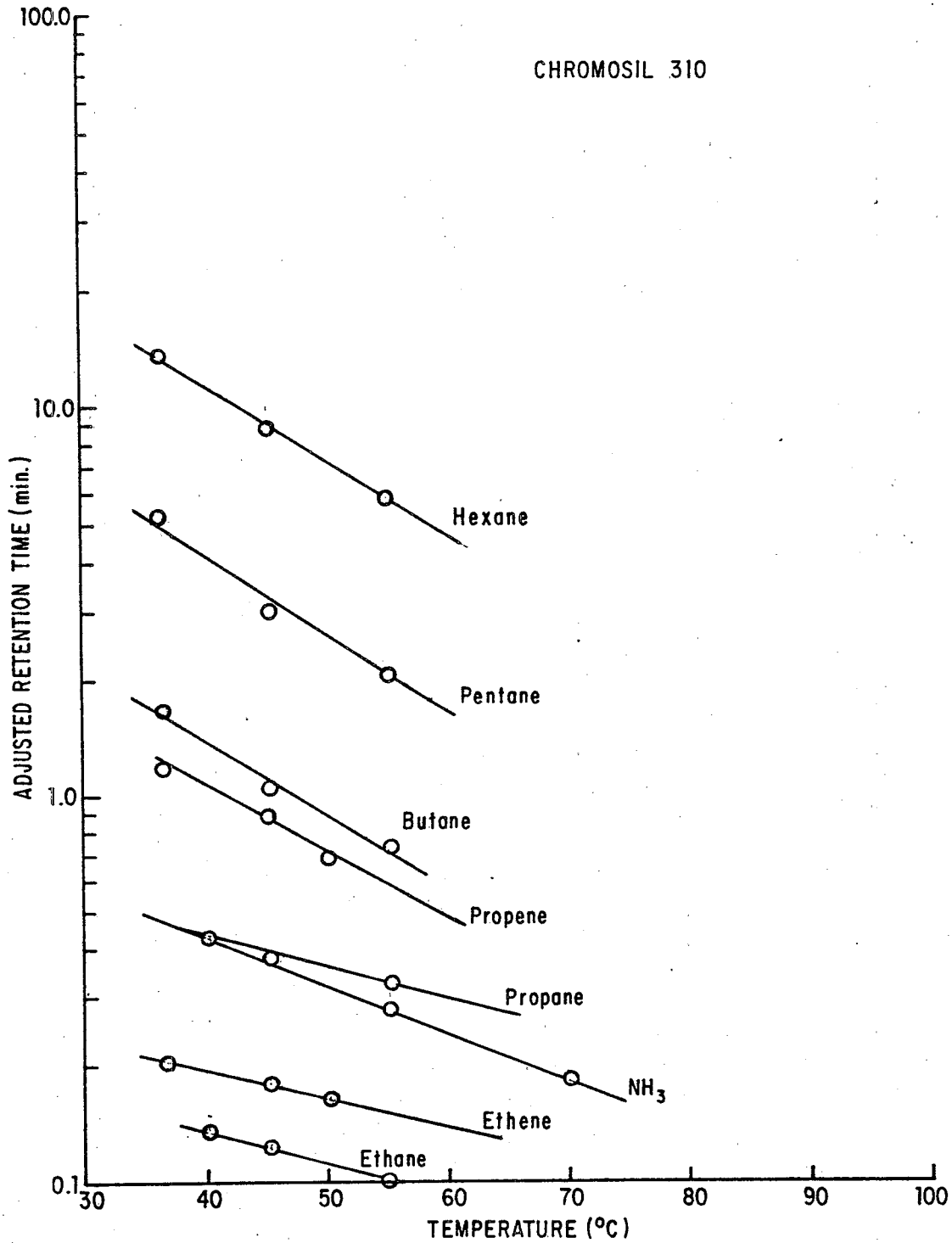


FIGURE 7-20

Retention times for hydrocarbons with Chromosil 310

because they eluted too late, over an hour at the temperatures shown. Figure 7-18 illustrates that most primary S compounds were separated with the possible exception of COS and $H_2S$. Comparing Figures 7-18 and 7-19 indicates that primary compounds are separated from the secondary group with the possible exception of methyl mercaptan and thiophene. However, comparing Figures 7-18 and 7-20 indicates that $H_2S$ falls between propane and propene, COS co-elutes with propane and ammonia, and $SO_2$ co-elutes with pentane.

As with the previous column it is not clear whether this column would be useful for the secondary group of compounds until additional possible compounds are considered. In addition, hydrocarbon interferences demand consideration before application of this column to the primary group analysis. However, on this column COS elutes before $H_2S$, a feature potentially helpful when measuring small amounts of COS in large amounts of $H_2S$. For this reason, this column was injected with actual retort gas to evaluate its usefulness for COS. However, with the ratios of COS to $H_2S$ found in retort gas, the two peaks could not be resolved.

Besides its inability to achieve the desired separation, this column also had other serious drawbacks. Its temperature limit (less than 70°C), can only be exceeded occassionally. Another problem is its sensitivity to water, which is abundant in retort gas. (The support for this packing is a silica gel.)

The next two columns to be evaluated were the Carbopack B HT 100 and the Carbopack B/1% XE 1.5% $H_3PO_4$. Of these two columns the latter packing is more difficult to prepare and, according to preliminary experiments, did not differ enough from the former column to warrant a separate investigation. This section therefore reports data only for the Carbopack B HT 100 column.

Retention time data for this column are shown in Figures 7-21 to 7-23. Of the columns examined thus far, this column gave the best separation of primary

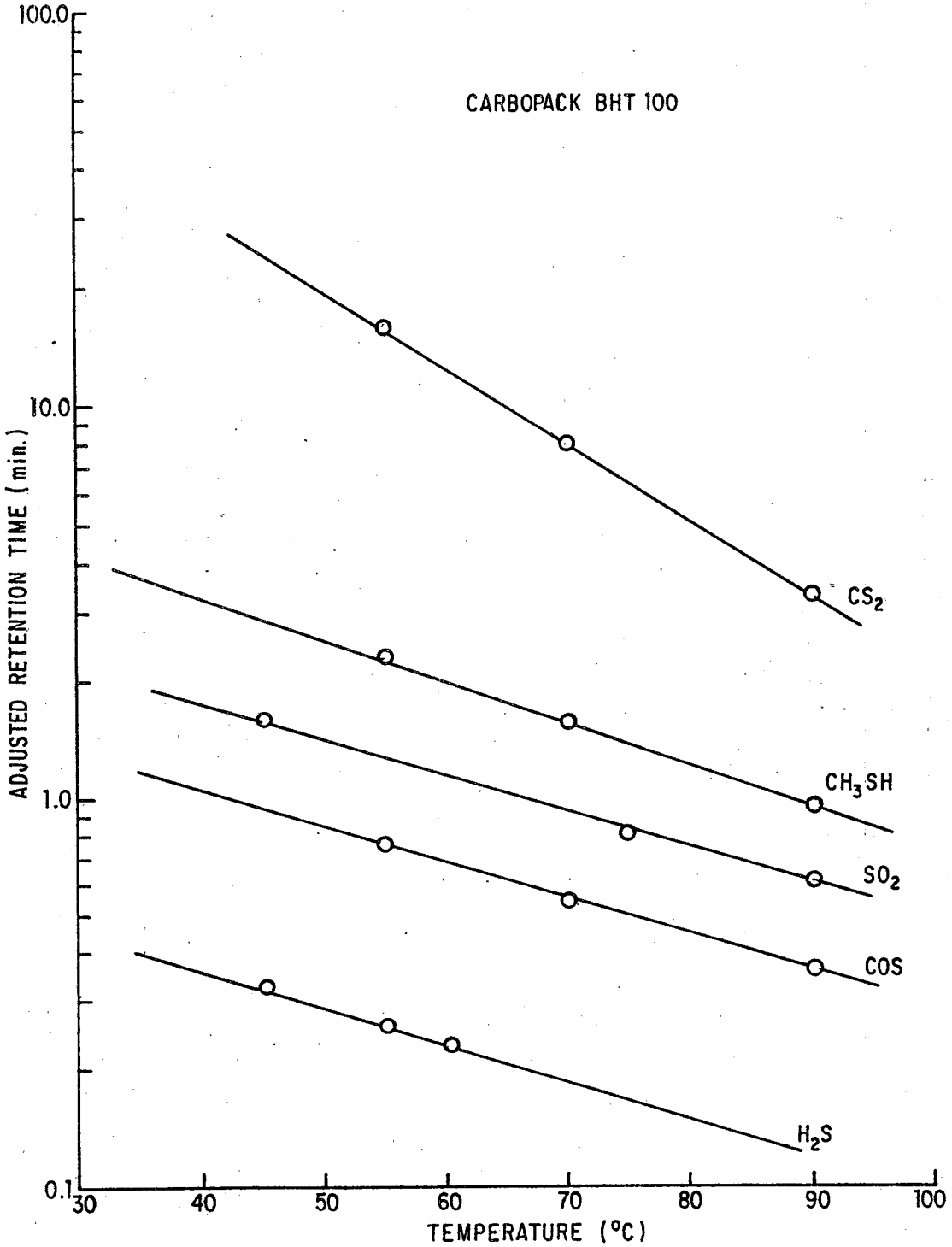


FIGURE 7-21

Retention times for the primary sulfur compounds with Carbopack BHT 100

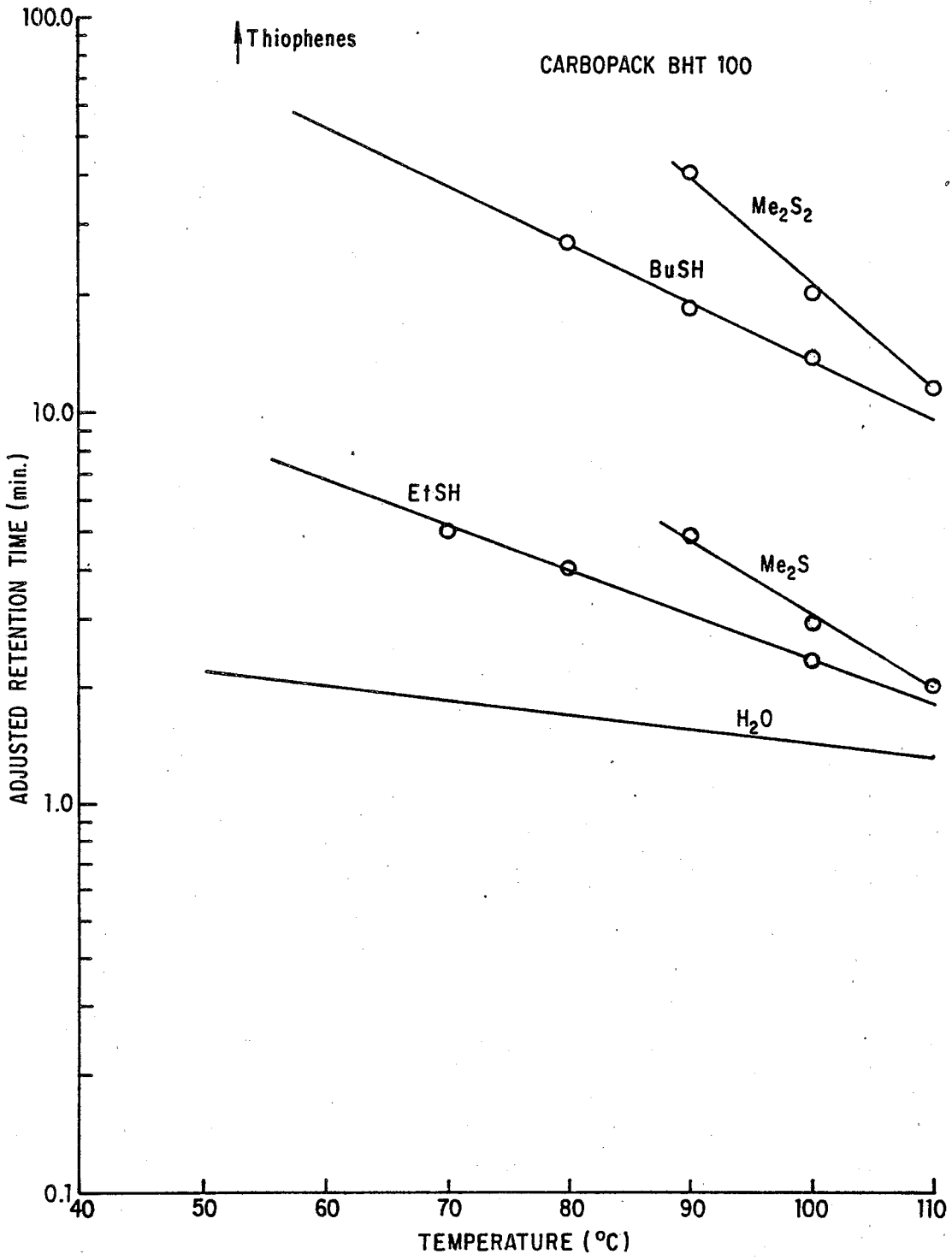


FIGURE 7-22

Retention times for the secondary sulfur compounds with Carbopack BHT 100

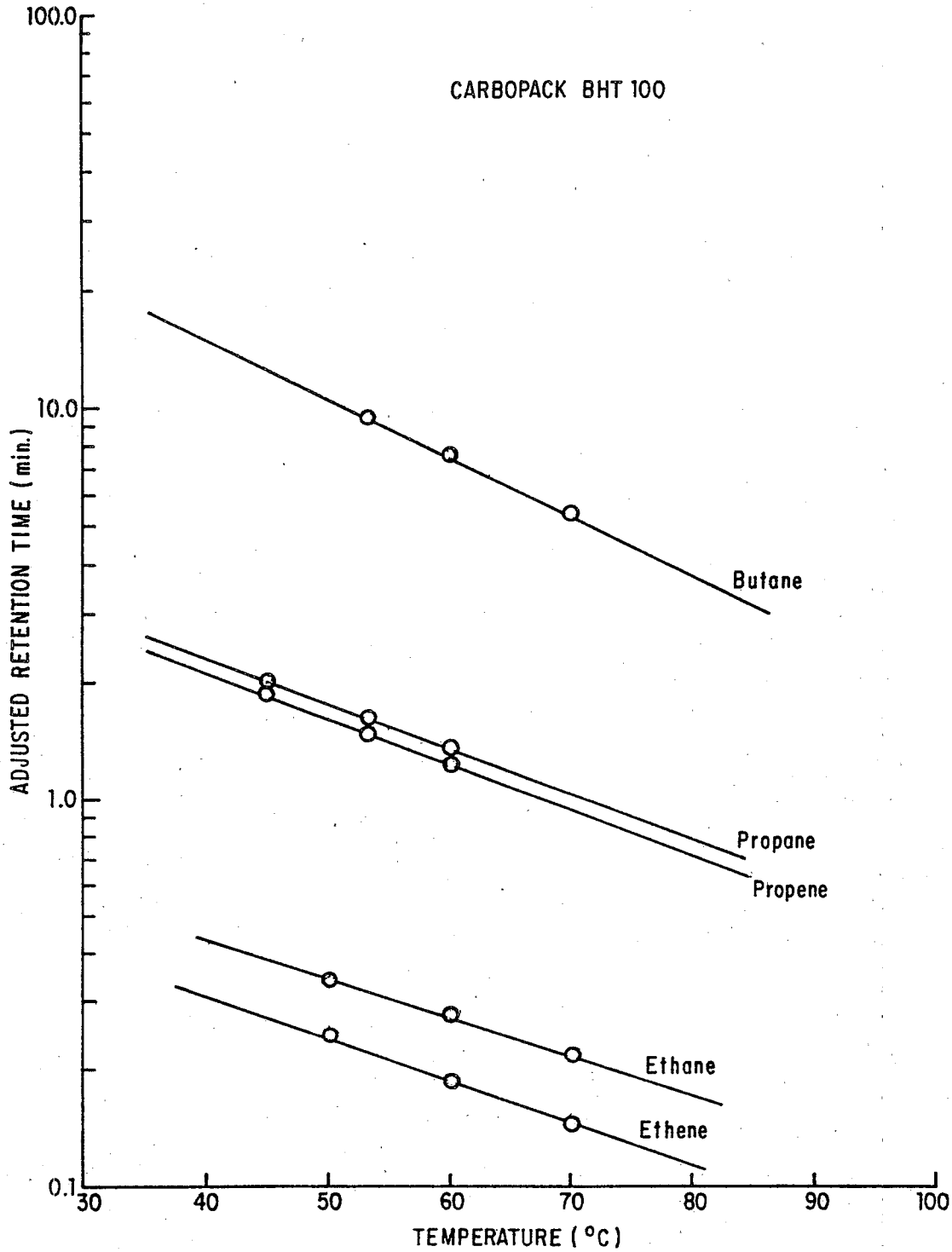


FIGURE 7-23

Retention times for hydrocarbons with Carbopack BHT 100

compounds. The wide separation of COS and $H_2S$ is especially encouraging in light of the large excess of $H_2S$ which is found in retort gas. $H_2S$ essentially co-elutes with the $C_2$ hydrocarbons, although this is not necessarily a problem in retort gas which contains high levels of $H_2S$ in the presence of small levels of ethane and ethene. $SO_2$ also elutes very close to the $C_3$ hydrocarbons and in the event that $SO_2$ is found in retort gas, it would be necessary to consider possible quenching effects on this species. Thiophenes, and likely other aromatic S species, do not elute from this column in less than one hour, and would therefore require a different column. The determination of $CS_2$ should also be approached cautiously with this column because of the proximity of dimethyl sulfide.

This column has also demonstrated other desirable characteristics, notably ease of packing, a wide temperature range, and tolerance to water. Water tolerance was examined by injecting 10 mg of liquid water onto the column. The column was "reconditioned" by temporarily raising the column temperature above the boiling point of water. When the temperature was again decreased to normal operating range, the retention times of COS and $H_2S$ were observed to have changed less than 0.3%, an insignificant amount. Considering that this amount of water would not normally be injected during the analysis of 1,000 retort gas samples, it was concluded that this column possessed more than sufficient tolerance towards water. Of the columns examined, the Carbopack B HT 100 column is clearly the best suited for the determination of the primary S species in retort gas.

Application to Retort Gas

The final test of any analytical method occurs when it is applied to an actual sample. Various columns and protocols were tested during operations of

oil shale retorts at the Laramie Energy Technology Center. Experiments at that site included:

1. A test of the acetone-washed Porapak QS column and protocol for the monitoring of $H_2S$. The objective of this effort was to determine the column longevity and stability, and to determine sampling problems.
2. Qualitative test of the remaining columns. The objective during this period was to determine which compounds could be observed with the columns of interest.
3. Quantitative monitoring of primary S species.
4. Quantitative monitoring of primary S species in support of the evaluation of a pilot-scale venturi scrubber during the May, 1982 operation of the 150 ton retort.

These tests were supported by the DOE (Contract Numbers DE-AS20-81LC10771 and DE-AS20-81LC10845), but are mentioned in this report because of their relevance to the subject at hand (Wallace and Sexton, 1982). During the first test, it was observed that $H_2S$ could be monitored routinely with the Porapak QS column. Retention times were stable, the flame in the FPD remained lit, and standards run during the period of the experiment varied less than 10% relative once the system was warmed up. These measurements were conducted with the valving and column arrangement shown in Figure 7-1 and described in more detail in the Protocol section of this chapter. Of particular importance was the observation that the column did not degrade even when exposed to uncooled (32°C) retort gas saturated with oils and water at that temperature (Wallace, 1982). The main problem encountered during this period was with the sampling system which permitted fluctuations in the process line pressure to affect the pressure and flow of sample at the chromatograph.

The results of the qualitative tests have been discussed in the column evaluation section of the preceeding text. In summary only the Carbopack B HT 100 column was capable of separating the primary S compounds. For most columns the separation of COS from a large excess of $H_2S$ was especially difficult.

The third experiment was conducted at the Low Void Volume Retort at the Laramie North Site facility. During this experiment the retort gas was analyzed simultaneously for S species by a GC/MS and for total S with the total S analyzer described in Chapter 6 of this report. Major species and hydrocarbons were also measured by a gas chromatograph, data which permitted the estimation of quenching effects whenever required. The primary S species were determined using the protocol described in the next section of this report with a Carbopack B HT 100 column. The objective of this test was to compare the results obtained by the different methods to determine the efficacy of each.

The objective of the test carried out during the operation of the 150 ton retort during May 1982 was to provide monitoring data to determine the efficiency of a venturi scrubber for the removal of $H_2S$ and other primary S species. This provided an opportunity to observe the performance of the sampling and analytical system described below. During this test, the primary sulfur species were monitored using the procedures described in the Protocol section of this chapter.

Figure 7-24 shows a chromatogram of retort gas obtained during this test, and Table 7-2 describes the detailed chromatographic conditions and integrator routines. Two injections were made to keep the compounds of interest within the dynamic range of the detector. The first was of 1 microliter for $H_2S$ 10 seconds before the integrator was started, and the second was of 100 microliters 7:00 minutes later. (Several changes in attentuation and chart speed

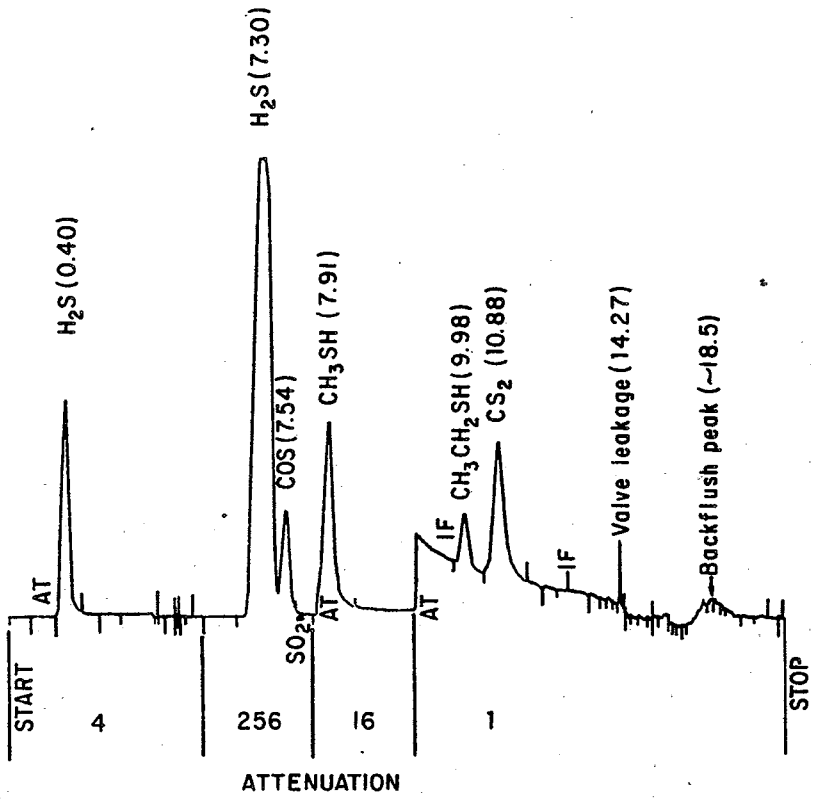


FIGURE 7-24

Chromatogram of retort gas sample: 6' x 1/8"
Carbopack BHT 100 at 65°C isothermal

Table 7-2

INTEGRATION AND VALVE SEQUENCING PROGRAMS FOR FIGURE 7-24

INTEGRATOR (HEWLETT PACKARD MODEL 3390)

| Time (min.) | Function |
|---|---|
| 0.00 | Attenuation = 8<br>Chart speed = 1.5<br>Peak width = 0.16 min.<br>Threshold = -1<br>Area reject = 500 |
| 0.10 | Intg. #5 (extend baseline horizontally) |
| 0.10 | Att 2↑2 (attenuation = 4) |
| 1.20 | Chart speed |
| 5.00 | Disable horizontal baseline extension |
| 6.75 | Attenuation = 256<br>Chart speed = 1.5 cm/min |
| 7.39 | Intg. #4 (disable automatic testing for solvent peak) |
| 7.87 | Attenuation = 16 |
| 8.75 | Chart speed = 0.5 cm/min<br>Attenuation = 0 |
| 9.10 | Intg. #2 set baseline at all valley points |
| 12.40 | Disable previous instruction |
| 14.00 | Chart speed = 0.3 cm/min. |

Table 7-2 (cont.)

PROGRAM ON CHROMATOGRAPH (BASELINE MODEL 1030)

| Item # | Time (min:sec) | Code | Operation |
|---|---|---|---|
| 01<br>02 | 00:01 | 13 | Inject 1 µl sample onto column 1 |
| 02<br>03 | 00:10<br>00:11 | 23<br>24 | Start integrator at 11 seconds |
| 04 | 01:00 | 14 | Backflush column 1 |
| 05 | 07:00 | 03 | Inject 100 µl sample onto column 2 |
| 06 | 12:00 | 04 | Backflush column 2 |
| 07<br>08 | 18:00<br>18:01 | 23<br>24 | Stop integrator |
| 09<br>99 | 29:45<br>00:30 | 99<br>00 | Repeat every 30:00 minutes |

CHROMATOGRAPHIC CONDITIONS

| | |
|---|---|
| Columns: | Carbopack B HT 100, 6' x 1/8" OD Teflon 2 each |
| Carrier flow rate: | 25 ml/min in each column, He |
| Column temperature: | 65°C |
| $H_2$ flow to detector: | 140 ml/min |
| Air flow to detector: | 180 ml/min |
| Detector: | Flame photometric operated in reverse mode |

occur to preserve the visual appearance.) $H_2S$, COS, methyl mercaptan, and $CS_2$ are plainly visible in the figure and occur well above the detection limit. Identification of these compounds was confirmed on site by injection of standards which yielded identical retention times. Their identities are also confirmed by the data in Figures 7-21 and 7-22 which indicate an absence of interfering compounds. Were it present, $SO_2$ would occur in the window between COS and methyl mercaptan; it is apparently absent in appreciable amounts. The peak labeled "$CH_3CH_2SH$?" was not confirmed by the injection of standards on site. However, it is the only known compound eluting during this time period, according to the work described earlier in this report, and is therefore very likely identified correctly in the figure.

Figure 7-24 illustrates that COS and to a lesser extent methyl mercaptan elute over a sloping baseline due to $H_2S$, and both the latter compounds must be determined with a tangent skimming procedure. For the chromatogram shown $H_2S$, COS, methyl mercaptan, and $CS_2$ occurred at concentrations of 3300, 62, 32 and 10 ppmv respectively, and should the proportion of $H_2S$ increase significantly, COS could not be determined under these chromatographic conditions. Although the separations during the May 1982 burn were conducted isothermally at 65°C, a better separation of $H_2S$ and COS can be effected by temperature programming. For example, through temperature programming between approximately 40°C and 120°C, the separation of COS can be improved significantly using an otherwise identical chromatographic system (Wallace, instruction manual prepared for the Laramie Energy Technology Center, 1982). However, temperature programming requires a considerable increase in instrument cost and complexity compared to isothermal systems. After due consideration of the types of samples expected, the analysts must therefore compromise between the better separation achieved with temperature programming and the lower costs of isothermal separation.

The sampling system which was used during the May 1982 test is shown in Figure 7-25, which also illustrates the auxiliary gas supplies and a system for generating and supplying calibration gas mixtures. This system was designed to provide a sample gas to the analyzers at a constant pressure and flow rate, and to remove excess water vapor and entrained material to prevent fouling of the analytical instruments. While it is likely that the system shown will be modified by the analyst to meet specific requirements, it is worthwhile to discuss briefly the functions of the various major components shown in the figure in order to illustrate the requirements of a sampling system.

Two sample conditioning and delivery systems, one for the inlet and the other for the outlet of a hypothetical treatment process, are shown in the upper left of Figure 7-25. The functions of the various components can be illustrated by considering only the top sampling train: the sampling probe, P1, consists of a 3/8 inch stainless steel tube which passes into the center of the process line to avoid collecting condensation which occurs on the duct walls. The first valve, V1, is included to permit the remainder of the sampling system to be removed and leak checked without breaking the seal to the process line. The condensers consist of two stainless steel vessels containing glass wool and immersed in an ice bath. Their function is to remove excess water vapor and most particulate matter. Additional filtering is provided by filters H1 and H2. All components discussed thus far are located next to the process line to avoid fouling the sample line which runs to the sampling trailer. During various tests it was discovered that pressure in the retort gas process lines often varied and sometimes became sub-ambient, a situation which made it impossible to rely on the process line pressure to force the gas through the sample line. For this reason a leakless, aluminum-head sampling pump, P1, was included to provide a constant flow. Valve V4 was included as an

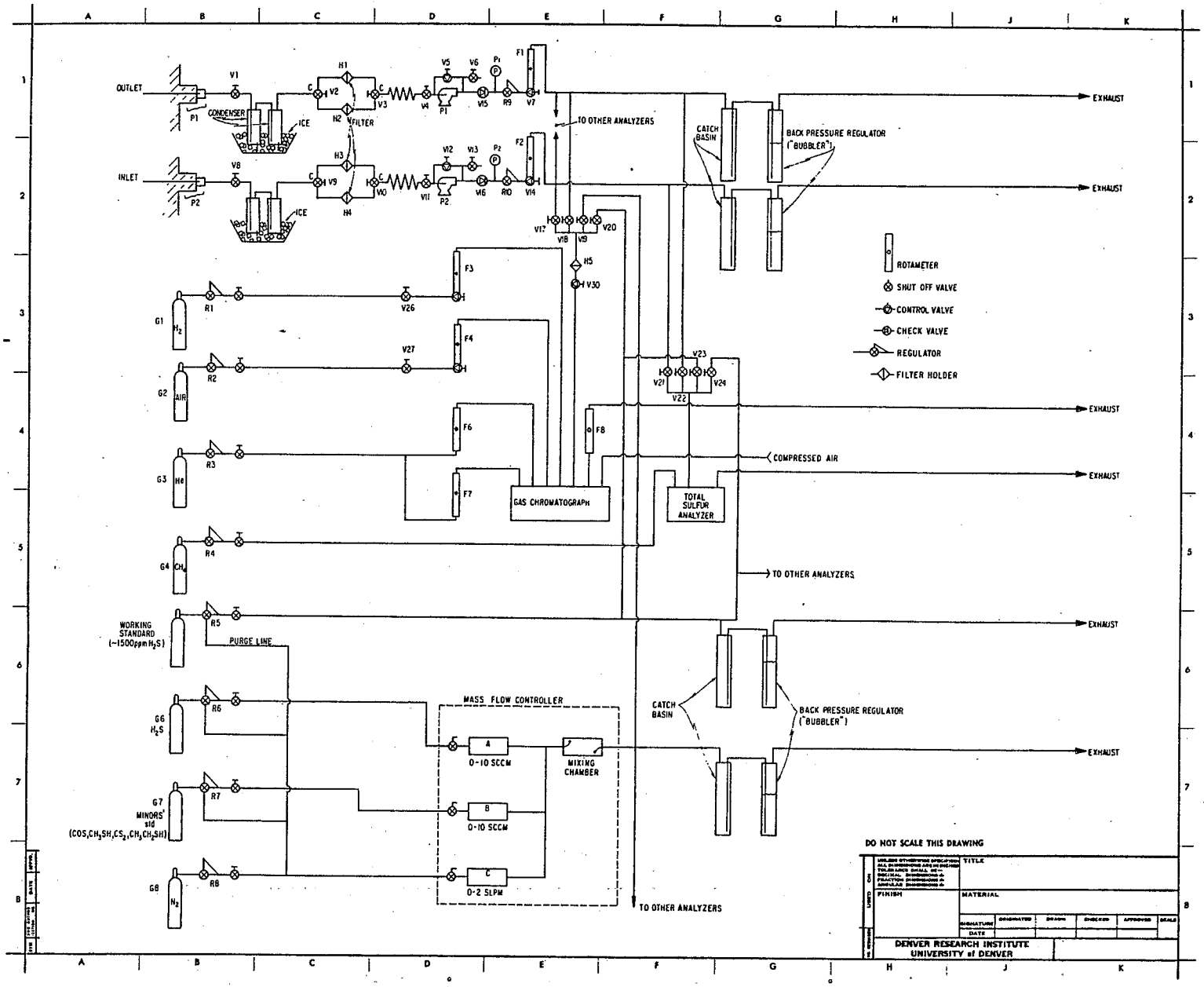


FIGURE 7-25

System for conditioning and supplying retort gas, standards, and support gases to various analyzers

aid in leak checking the downstream portion of the sampling system. Check valve V15 was included to prevent backwards flow during periods of negative pressure in the process line. The back pressure regulators shown consist of acrylic tubes containing a column of water through which the sample gas must pass before exhausting to the atmosphere. Although mechanical back-pressure regulators were also tested, they did not prove reliable. Two main problems became apparent with the back pressure regulators shown in the figure. First, if a vacuum were inadvertently applied to the sample line, (e.g., due to pump failure), the water in the regulators would be pulled back through the entire system. This problem was solved by including two acrylic columns in line, the upstream column acting as a catch basin for any overflow. Second, pressure fluctuations in the process line still affected the analyzers, even with the pressure regulators in place, albeit to a lesser extent. This phenomenon was further minimized by including pressure regulator R9 and rotameter F1 for the purpose of measuring and maintaining a constant flow rate through the sample line.

In order of operation, the flow rates are first set by opening valve V1 with the pump running. With valve V7 fully open, valve V5 is adjusted to give slightly more than the desired flow rate. The flow rate is trimmed by adjusting regulator R9 to cause a slight lowering of the pressure, and further adjusted with valve V7 to achieve the desired flow rate. The system is next leak checked by plugging the inlet of the sample probe. The system is considered leak tight if no flow is apparent at the flow meter F1.

If the gas chromatograph is connected directly to the sample line, the entire pressure drop occurs across the 1/16" tubing which is contained therein. With this arrangement small changes in the sample line pressure, or small changes in the resistance of portions of the 1/16" tubing cause pressure

changes in the sample loop and, therefore, changes in the calibration of the chromatograph. Such effects are minimized by decreasing the flow through the chromatograph with control valve V30. The flow rate should be set fast enough to sweep out the sample delivery valves V17 through V20 and filter holder H5. The flow through the chromatograph is monitored by a rotameter F8 and should remain constant for different samples and standards.

The sampling system shown in Figure 7-25 was developed in response to the practical exingencies of field sampling, and certain questions remain to be addressed. For example, "What components are lost during the cooling step, at which point the gases are exposed to an alkaline water solution?" It is also of interest to consider what fraction of the sulfur pollutants are present in the particulate as opposed to the gaseous phase in the sample stream. Potential methods for improving the reliability and integrity of the sampling method are presently under investigation.

Figure 7-25 illustrates two approaches to providing standards, a mass flow system and pre-mixed gas bottles. The former provides a range of concentrations to bracket the sample concentrations, while the latter provides a fixed standard for occasionally checking the operation of the analyzers. This dual arrangement is convenient when operating more than one type of analyzer, each on a different calibration schedule. For mass flow controllers with the ranges indicated in the figure, $H_2S$ standards can be generated in the range 500-100,000 ppmv starting with pure $H_2S$. For preparing standards for the minor gases, it is necessary to start with more dilute mixtures, typically in the range 0.1-1.0% v/v.

PROTOCOL FOR DETERMINATION OF HYDROGEN SULFIDE, CARBONYL SULFIDE, SULFUR DIOXIDE, CARBON DISULFIDE, METHYL MERCAPTAN, AND ETHYL MERCAPTAN IN RETORT GAS

Principle

The above mentioned sulfur species, referred to hereafter as the primary S species, are determined by gas chromatography with flame photometric detection. The concentration range of interest in retort gas is covered by using two sample injection valves with different injection volumes.

Interferences

Hydrocarbons, which co-elute with the S species of interest, alter the fluorescent S signal if present in excess. For the procedure described herein, this interference is addressed by proper selection of column and detector. In the case of the single flame detector (SFPD) the operating mode also affects the likelihood of interferences.

Using the column recommended in this section, $H_2S$ co-elutes with ethane and ethene. However, with a one microliter injection volume, 1,000 ppmv of $H_2S$ can be determined in 10% ethane without measurable error by using the single flame detector in the reverse mode and by calibrating with peak height. Higher levels of ethane can be tolerated with a dual flame detector (DFPD). If the sample volume is increased to higher values to detect lower levels of $H_2S$ or other minor S species, less ethane could be tolerated. However, with the concentrations of $H_2S$ normally found in retort gas, it is unlikely that such interferences would be a problem.

With the column recommended below, $SO_2$ elutes very close to the $C_3$ hydrocarbons. In the event that $SO_2$ is detected in retort gas this interference should be considered. However, as of this writing, $SO_2$ has not been found in any retort gas of which the authors are aware.

In addition to the above-listed compounds, it must be recognized that there are numerous additional S compounds which have a high enough vapor pressure to be found in retort gas. Listing the $C_2$ to $C_4$ mercaptans, sulfides and disulfides, in addition to the thiophene and methyl thiophenes, one can easily generate a list of 20 such compounds. In general, these compounds will elute after the above-named compounds. However, $CS_2$ elutes close to dimethyl sulfide, and the elution times of both compounds should be established with standards.

Equipment

1. Gas chromatograph. The gas chromatograph should be equipped with two gas sampling valves and a flame photometric detector. The necessary arrangement of valves and columns is shown in Figure 7-26.

   The sample injection volumes must be selected for the concentrations of S species encountered, and the injection volumes should be changed on site should unexpected concentrations be encountered. With a packed column, a 1 microliter injection volume covers the range 500-20,000 ppmv, which is adequate for monitoring $H_2S$ in retort gas from most indirect retorting processes. A 50 microliter sample loop is typically adequate for the range 10-200 ppmv, the concentrations of minor gases encountered in the same type of gas. It is most convenient if the sample valves are operated from an automatic timer.

2. Integrator. If the separation is carried out isothermally, (see below) it is essential that the integrator be capable of tangent-skimming COS from the tale of the $H_2S$ peak. Alternatively, the integrator can be replaced with a dual-pen, dual-range strip chart recorder. However, a peak integrator has the advantages of a

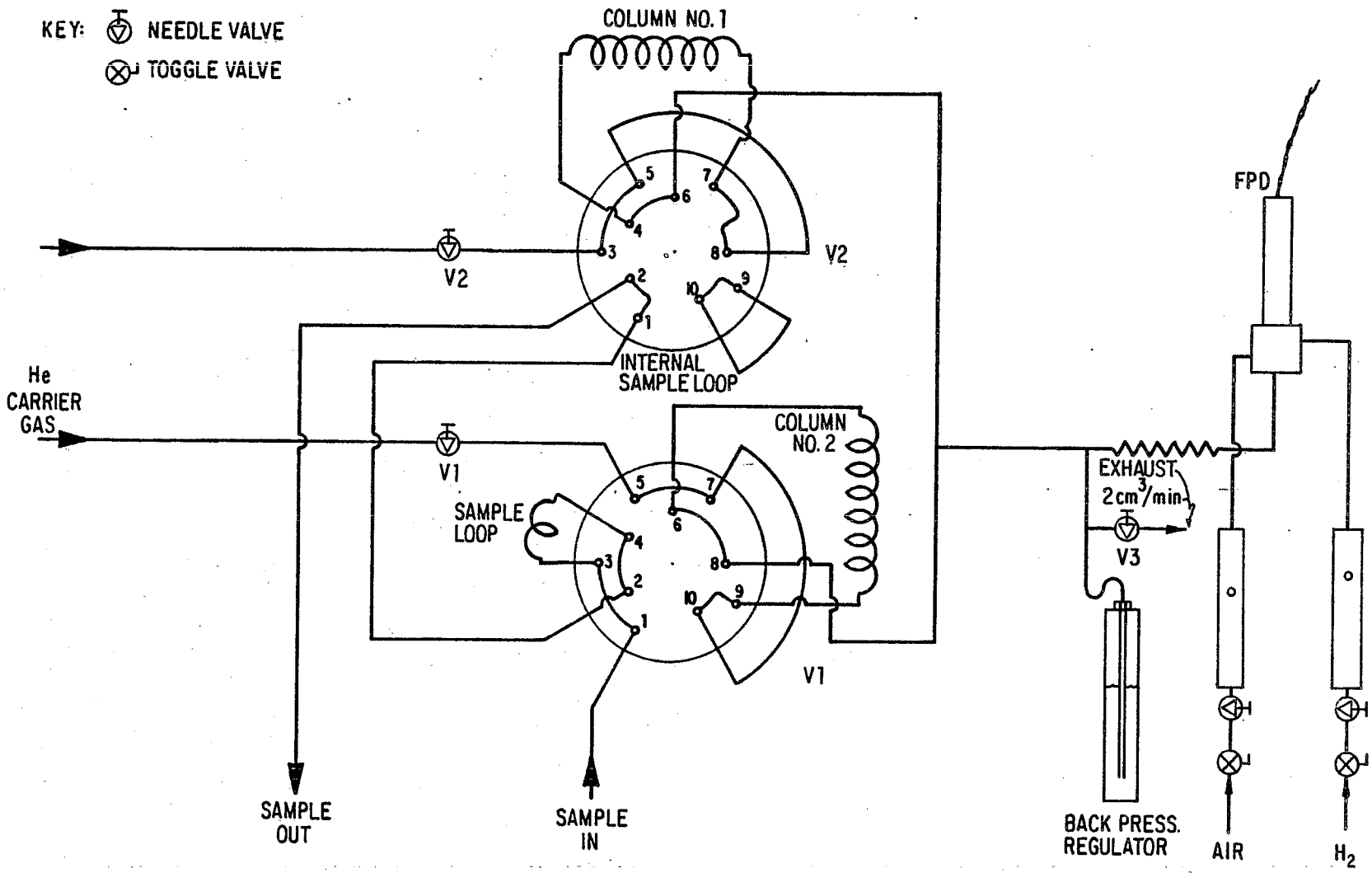


FIGURE 7-26

Column and valve configuration for monitoring sulfur species in retort gases

wider dynamic range, automatic printout, and programmable control of the valves.

3. Columns. Two columns are required, one for each injection valve. A 1/8" od X 6' column of Carbopack B HT 100 is adequate for most compounds, including $H_2S$, COS, $SO_2$, methyl mercaptan, ethyl mercaptan and $CS_2$. Thiophene does not elute from this column in a reasonable time and must be determined with a different column (e.g., Chromosil 310). It is not clear at this time whether later eluting compounds can be uniquely identified on the basis of their retention time using a packed column.

4. Detector. A flame photometric detector is required to distinguish among the S species and the other numerous gases found in retort gas. Of the FPD's available, the dual flame model is least prone to interferences due to co-eluting hydrocarbons. The single flame model is more prone to interferences, although it may be applicable for certain types of retort gas. (See previous text.) Hydrocarbon quenching effects in the single flame FPD are minimized by reversing the hydrogen and oxygen flows so that the air is introduced concentric to and interior to the flow of hydrogen. However, in this configuration the flame is often difficult if not impossible to ignite.

5. Mass Flow Controller. Mass flow controllers are needed for blending gas standards. A set of two controllers which operate in the range 0.5-10.0 SCCM plus one controller in the range 50-1,000 SCCM are convenient. Connect as shown in Figure 7-25.

Standards

Standards should be prepared which bracket the concentrations of the S species found in the retort gas. This is most easily achieved by mixing standards on site using a set of mass flow controllers.

Calibrate each of the mass flow controllers against a volumetric standard which is traceable to an NBS standard. The following procedure is applicable to the 1,000 SCCM mass flow controller. Calibrate the stop watch against an NBS time base which is available on most telephone exchanges.

A dry test meter is required for calibrating the 1,000 SCCM channel, while the 10 SCCM channels require a small bubble meter. The following procedure is written in terms of the dry test meter, although the procedure is identical for the 10 SCCM channels with the substitute of the bubble meter in place of the dry test meter:

1. Leak check. Connect a supply of $N_2$ to the inlet of the mass flow controller and the dry test meter to the outlet. Block the exit from the dry test meter with a leak-tight seal and pressurize slightly with $N_2$. Adjust the mass flow controller to its maximum rating. (CAUTION: Do not exceed the pressure rating of the dry test meter.) The mass flow controller should read zero flow. Back off the regulator to a lower pressure. The pressure at the regulator should remain constant.

2. Calibration. Remove any restrictions from the exit of the dry test meter. Set the flow rate on the mass flow controller and allow a reading to stabilize. Determine the volumetric flow rate by measuring the time required for an integral number of revolutions of the dry test meter. Adjust to standard conditions. Repeat for several flow rates spanning the intended range of use.

It is recommended that flow rate calibrations be conducted with the gas to be monitored. However, in the case of certain reactive gases such as $H_2S$, this is not presently possible with available equipment. For example, the fluid in a bubble meter absorbs a large percentage of the flow of $H_2S$, while dry test meters are not practical at the low flow rates required for $H_2S$. For such gases, the mass flow meter must be calibrated with $N_2$, and then converted to $H_2S$ using conversion factors which are calculated from the molar weight and heat capacity.

Procedure

Typical chromatographic conditions for an isothermal separation are listed in Table 7-2. However, chromatographic conditions may need to be adjusted somewhat to take into account differences among samples. In particular, separation of COS from the tail of $H_2S$ can be improved by starting the column temperature at approximately ambient and increasing after the elution of methyl mercaptan.

Calibrate the chromatograph over the entire range of interest to determine the linear range of the system. Plot the square root of the peak height against concentration.

Inject a sample under identical flow rate and pressure as the standard and note the peak height of each component of interest. Bracket the peak heights of the sample by the heights of the standards. Determine the concentration by comparison to the calibration plot described in the previous paragraph.

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## SECTION 8

## CONCLUDING REMARKS

In addition to the tests investigated explicitly during this program, several other measurements have been employed for the routine analysis of retort effluents, an experience which has provided worthwhile information on many procedures. While such information does not justify its own chapter, it is nevertheless helpful to the analyst. During the period of this investigation, information on additional methods has also be described by contemporary investigators. The purpose of this section, therefore, is to summarize the available information on methods of analysis for oil shale effluents which should be important to the wastewater engineer.

The pH of retort water is determined almost universally by application of the pH electrode. In the authors' laboratory this method is applied routinely without major problems. However, certain procedural precautions are necessary to obtain the best results. First, the glass membrane becomes fouled easily when working with oily waters in general and retort waters in particular, which results in drifting and inaccurate response. (The electrode response can be restored by following the manufacturer's instructions for this purpose, which normally involves washing the electrode with a strong detergent.) This means that the calibration and response of the electrode must be checked both before and after a series of measurements with at least two buffer standards; a degraded response at the end of the series requires that all analyses be repeated. It should also be realized that the pH of retort waters is temperature dependent. For example, the pH of one set of retort waters examined varied 0.024 pH units/°C. While many pH meters are equipped with a "TEMPERATURE" control, this typically adjusts only the Nernstian slope and does

not compensate for the effects discussed here. Thus, in order to obtain pH values which are accurate to ± 0.1 pH unit, the temperature should be controlled to better than ± 4°C; in order for the reported pH to be meaningful, the measurement temperature must also be reported.

In the authors' experience, when these precautions are taken pH measurements on retort water are normally precise to ± 0.1 pH units, which is the limit of readibility for the pH meter in use. While the absolute accuracy of this measurement has not been established by reference to an independent method, it is noteworthy that when ion balances were calculated on one set of dilute samples using pH measurements so determined, the balances were within experimental error. (See below.)

Similar comments can be made regarding the measurement of electrical conductivity (EC). As with the pH electrode, the conductivity probe is easily fouled and needs to be cleaned periodically according to the manufacturer's instructions. In order to assure that the cell has not been fouled during a series of measurements, it is necessary to analyze a KCl standard both before and after and to discard any analyses if the calibration has changed. The analyst should also be aware that the temperature coefficient for the EC measurement is different for retort waters than for most surface and ground waters. For example, for one set of retort waters the EC varied approximately 4%/°C, while the conductivity of most surface waters varies approximately 2%/°C. Many of the commercially available conductivity meters are equipped with a temperature compensation control which corrects the conductivity 2%/°C, which would obviously be inappropriate for retort waters. It is therefore recommended that retort waters be equilibrated to a fixed temperature, say 25°C, before the EC is measured, and that this temperature be reported with the conductivity results. It should also be noted that the EC does not necessarily

vary linearly with concentration in high-ionic strength waters so that using EC as an indication of total dissolved ions is not as accurate for retort waters as for more dilute surface and ground waters.

Alkalinity, which is defined as the amount of strong acid required to lower the pH to certain end points, is often interpreted in terms of the amount of carbonate and bicarbonate. While such an interpretation is usually correct for surface and ground waters, it is incorrect for most retort wastewaters because of the presence of $NH_3$, which consumes a portion of the acid titrant. Examination of a typical titration curve of an oil shale wastewater (Figure 8-1) indicates the absence of clear end points and emphasizes the difficulty of determining carbonate species by this method. Instead, it is recommended that inorganic carbon (carbonate + bicarbonate) be determined by the instrumental methods that are used for total organic carbon.

Total inorganic carbon (TIC), which in retort waters is equivalent to carbonate + bicarbonate, is determined instrumentally by acidifying the sample and purging the resulting $CO_2$ into a detector. Total carbon (TC) is determined similarly by combusting or rigorously digesting the sample to convert all organic and inorganic carbon to $CO_2$. Commercially available instruments typically combust the sample in an oxygen stream or digest it in strong chemical oxidants; detection is by coulometry, infra-red absorption, or flame ionization after conversion to methane. Several variations of these procedures are available: total organic carbon (TOC) can be determined "indirectly" by measuring TC and TIC separately and calculating the difference, or "directly" by acidifying the sample in order to remove the inorganic carbon prior to injection into the instrument. If the sample is filtered through a 0.45 micrometer filter prior to injection, the resulting measurements are

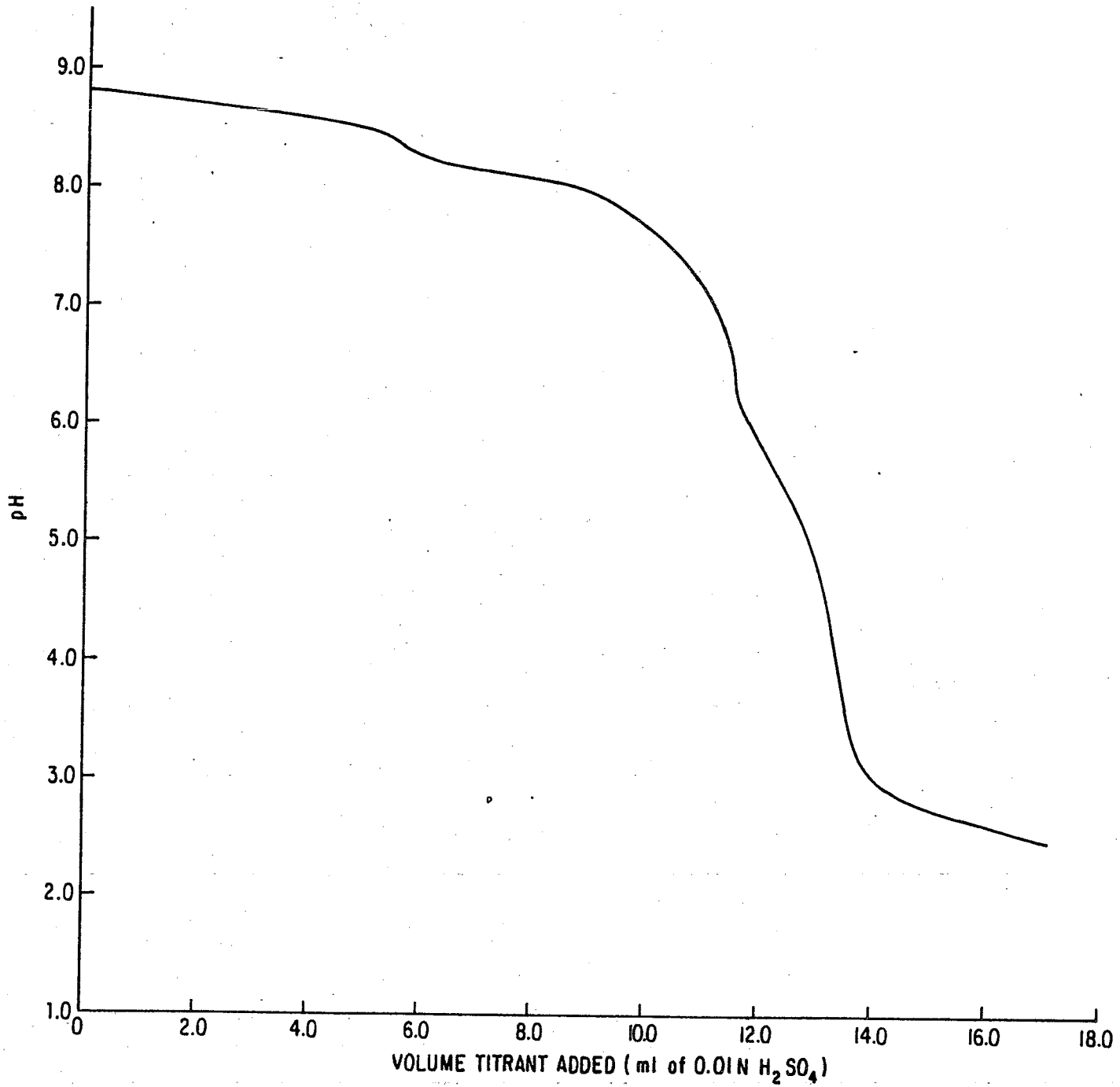


FIGURE 8-1

Titration curve for a retort water sample

referred to as dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), and dissolved total carbon (DTC).

Although TOC and TIC are important measurements, they have not been addressed during the experimental phase of this study because of concurrent investigations being carried out at other laboratories. In the authors' laboratory TOC and TIC measurements have been carried out routinely in the support of various pollution control programs, and the quality control procedures applied during these tests have provided some insight into the problems which can occur with these procedures. For example, with an instrument using an infra-red detector the reproducibility for the measurement of TIC and TC measurements for retort waters analyzed under field conditions was approxiamtely 10% relative. Thus, when determining TOC by difference, the errors generated by taking the difference between two large numbers can be substantial. Applying the common formulas for propagation of error indicated that for retort waters the error in the TOC measurement varied 15 to 100%, depending on the relative concentrations of TIC and TC. During this same investigation, however, no evidence of analytical bias was observed and the recovery of added TIC was 120%, which is reasonable for the precision of the technique used (Habenicht et al., 1980). TIC measurements have also been performed under similar conditions by coulometric titration with a routine precision at 1% relative (one $\sigma$). These data illustrate the importance of applying quality control and statistical interpretation during the determination of TOC and TIC, and of reporting the precision of the results along with a statement regarding the method by which the precision was determined.

Others who have studied the determination of TOC and TIC more thoroughly have arrived at similar conclusions. For example, an interlaboratory comparison including 18 laboratories has been carried out using retort and

synfuel wastewaters along with identical samples which had been spiked with known quantities of TOC. A variety of analyzers was applied, including those with infra-red, coulometric, and flame ionization detectors. The results from this study indicated that there was no significant difference between the results obtained with the various types of analyzers. The recovery of the spiked standards was essentially 100%. However, those analyzers equipped with coulometric detectors were the most precise. Standards of known composition were also included in this study to determine which laboratories were capable of measuring TOC in pure solutions at concentrations encountered in retort waters, and the results of three laboratories were rejected on this basis. The results from these standards also indicated that many laboratories had difficulty quantitating high level samples. Thus, those laboratories capable of analyzing pure samples were normally capable of analyzing retort waters. These investigators thus concluded that "most of the problems associated with the analysis of these samples are due to technique and not the TOC method itself," and provided a list of 9 suggestions for best results (Jackson, personal communcation, 1982). These included suggestions for volumetric dilution, careful application of quality control procedures such as replications and spikes, vigorous stirring, and practice with very high level standards.

In a separate study, Langlois et al. (1982) compared the TOC determinations obtained with two different oxidation processes, the first consisting of high temperature oxidation in $O_2$ and the second consisting of a photochemically assisted oxidation in persulfate solution. A coulometric finish was employed in both cases.

Of the 17 pure compounds tested, 15 gave equivalent results by both methods while two gave incomplete recovery by the photochemically assisted

procedure. However, for the 9 retort wastewaters examined equivalent results were obtained, indicating that the most refractory compounds were not significant sources of error in retort water. DOC was determined both by difference and directly, and no bias between the two methods was observed. However, the direct method was the more precise. The precision of these analyses was approximately 1% relative ($1\sigma$). Compared to the other finishes available, the coulometric method was preferred by these authors because of a wider dynamic range, a higher upper limit, and more stable calibration. In summary, the available evidence suggests that the existing methods for measuring TOC and TIC in retort wastewaters are adequate and that acceptable results can be obtained by considering the guidelines mentioned in these paragraphs. The data discussed herein also suggest that the coulometric titration is the preferred finish.

In the authors' opinion there is not yet a proven method for the determination of total nitrogen in retort water. The same statement therefore applies to organic nitrogen, which is defined as the difference between total and ammoniacal nitrogen. This deficiency may be important because organic bases are abundant in retort water, and it would be helpful to be able to establish their total concentration as a quality control parameter. Two methods are presently in use for the total nitrogen measurement: (1) the well-known Kjeldahl method, and (2) combustion followed by the chemiluminescent detection of the NO produced. The problem with the first method is that the more refractory compounds are incompletely digested (although this can often be alleviated by the addition of catalysts and the use of higher temperatures), and that the method is slow and cumbersome for field use.

The second method was investigated during the first phases of this project, and was shown to give different responses for different compounds

(June, 1980 Progress Report). That is, the conversion efficiency to NO was compound dependent, especially for azo- and nitro-compounds. Similar findings have been reported in the literature for this method (Drushel, 1977). Whether or not this is significant for retort waters has not yet been determined.

In addition to the tests which are performed for the purpose of evaluating pollution control equipment, certain other tests are helpful to the analyst for the purpose of checking the correctness and completeness of the individual determination. One such procedure is the calculation of the ion balance, that is, the electrical balance between the anions and cations which have been determined. Here the ion balance, B, is defined

$$B = 2\frac{\Sigma_C - \Sigma_A}{\Sigma_C + \Sigma_A}$$

where $\Sigma_C$ and $\Sigma_A$ indicate the absolute values of the cationic and anionic charges respectively. Since the true ion balance is always zero, incorrect or incomplete analyses are reflected in non-zero values for B. In practice the major cation ($NH_4^+$) and anions ($CO_3^=$, $HCO_3^-$) are not measured directly, but are calculated based on measurements of total ammonical N, total inorganic carbon, and pH. Thus, errors in any of these measurements result in non-zero balances.

The principal difficulty with the ion balance calculation is due to the buffering capacity of retort waters. That is, a small change in pH causes a large change in ionic concentrations. This problem can be illustrated for a water containing 100 mM ammonical N and 45.84 mM total inorganic carbon. At a pH of 9.25, the ion balance would be 0.00, assuming ideal solution behavior. However, if the pH were measured incorrectly high by 0.1 pH units, which

represents a reasonable error during routine analysis, the calculated ion concentrations would change as follows:

| | $NH_4^+$ + | $CO_3^=$ ——> | $NH_3$ + | $HCO_3^-$ |
|---|---|---|---|---|
| pH = 9.25 | 50.00 mM | 4.17 mM | 50.00 mM | 41.67 mM |
| pH = 9.35 | 44.26 mM | 5.13 mM | 55.74 mM | 40.71 mM |

For a measured pH of 9.35 the resulting ion balance would thus be -14%. Thus, small errors in pH measurement thus contribute to large imbalances.

A second precaution regarding the ion balance is related to the high ionic strength of many retort waters. The calculations described in the previous paragraph are strictly correct only at infinite dilution and become less accurate as the ionic strength increases. In theory, this problem can be alleviated by simply diluting the sample before measuring the pH which is used in the ion balance calculation, a procedure which can result in a slightly different pH than is obtained with an undiluted sample. This is illustrated by analyses performed in the authors' laboratory on a set of 15 samples. Ion balances were normally within ±15% for samples containing less than 30 meg/l of $NH_4^+$. For samples containing approximately 100 meg/l of $NH_4^+$, ion balances were in error by approximately 80%. However, when the latter samples were diluted and the pH of the diluted solution was used in the calculation, more reasonable ion balances were achieved (Shaffron and Wallace, 1982).

Although electrical conductivity is often used to check the determinations of total ionic species, it is obviously subject to the same problems inherent in the ion balance calculation. While both of these determinations are useful for retort waters, they are obviously best applied to diluted samples. A measurement of pH more accurate than the normal ± 0.1 pH units would also improve the quality of these calculations.

Table 8-1 summarizes the recommendations of this report for methods of chemical analysis for oil shale wastewaters and product gases. Combusted gas

Table 8-1

RECOMMENDED PROCEDURES FOR THE ANALYSIS OF OIL SHALE EFFLUENTS

| Species | Recommended Methods |
|---|---|
| **WASTEWATERS** | |
| pH | pH electrode |
| Electrical conductivity | Conductivity cell |
| Total dissolved material | Freezing point depression |
| Sulfide ($HS^-$ + $S^=$) | Pontiometric titration with Pb(II) |
| Total ammoniacal N, (Na,K)[a] | (1) ion chromatography<br>(2) modified electrode method |
| Aqueous $NH_3$ | UV absorption of headspace |
| Inorganic C ($HCO_3^-$ + $CO_3^=$) | Evolution of $CO_2$ from acidified sample; coulometric finish |
| Total organic carbon | Combustion or UV assisted chemical oxidation to $CO_2$; coulometric finish |
| Ion Balance | Calculate based on pH of diluted sample |
| Total S | Oxidation with $H_2O_2$ followed by determination of $SO_4^=$ |
| Anionic species: $S_2O_3^=$ $SCN^-$, $NO_3^-$, $SO_4^=$, $SO_3^=$, $PO_4^{3-}$, $NO_2^-$ | Ion Chromatography |
| **RETORT GAS** | |
| Total S | Continuous combustion followed by measurement of $SO_2$ |
| Individual S species: $H_2S$, COS, $CH_3SH$, $CS_2$, $CH_3CH_2SH$, $CH_3CH_2CH_2SH$, $CH_3(CH_2)_2CH_2SH$, thiophene | Gas chromatography with flame photometric detector, using procedures detailed in text. |

[a] When using ion chromatography, Na and K can often be determined simultaneously with $NH_4^+$. However, if $NH_4^+$ need not be measured, more convenient methods are available for K and Na (Wallace, 1981).

streams have not been treated because of their similarity to utility and industrial stack gases which have already been studied exhaustively. For information on additional methods, such as minor and trace elements, the reader is referred to the first report prepared for this project (Wallace, 1981). While these proposed methods have been tested to varying degrees with actual retort samples, it must be realized that wider application will inevitably lead to new information and refinements. The authors of this report would appreciate such information as it is developed by practitioners.

In conclusion, it is worthwhile to emphasize the importance of quality control and quality assurance in applying these methods to oil shale effluents. Although a laboratory may have control charts and statistical interpretations based on their experience with a variety of surface and ground waters, these data should not necessarily be applied to retort samples. Statements of precision and accuracy should be based on experience with actual retort samples, not on experience with related samples or on the repeatibility of standard solutions. In order to obtain the best estimate of the precision, samples should be repeated, not sequentially, but spaced at intervals throughout the day in order to include contributions from instrument drift (at least for stable species). Standards should also be run both before and after a series of analyses in order to be sure that the instrument did not change during exposure to retort samples. It is, of course, recommended that the analyst first practice with a previously characterized sample whenever possible.

Because many of the species of interest in retort wastes are unstable, it is important that the analyst attempt to establish the integrity of the sampling methods and not simply rely on published guidelines. For this purpose it is recommended that the sampling and preservation techniques appearing in

the literature be a starting point, but that decay studies be an integral part of any sampling and analysis program. If the efficacy of the sampling and preservation techniques cannot be established for the particular samples in hand, it is recommended that analyses be completed immediately on site. Finally, the analytical report should include a quality assurance section specifying not only such parameters as precision and recovery, but the exact method by which they were determined.

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

Several methods of chemical analysis are described for oil shale wastewaters and retort gases. These methods are designed to support the field testing of various pollution control systems. As such, emphasis has been placed on methods which are rapid and sufficiently rugged to perform well under field conditions. Ion chromatograph has been developed as a technique for the minor non-carbonate inorganic anions in retort water, including $SO_4^=$, $NO_3^-$, $S_2O_3^=$, $SCN^-$, and total S. Acetate, $Cl^-$, $NO_2^-$, $SO_3^=$, and $PO_4^{3-}$ can be observed with this technique but cannot necessarily be separated if present simultaneously. The method recommended for sulfide is a potiometric titration with Pb(II). $SCN^-$, $S_2O_3^=$, $SO_4^-$, $Cl^-$, $CO_3^=$, $NH_3$, and $OH^-$ were shown to not interfere with this technique. The freezing point depression is used to determine the total solute content in retort waters, a test which can be considered analogous to the standard residue test. Three methods are described for the determination of total ammoniacal nitrogen in retort wastewaters: (1) a modified ion selective electrode technique, (2) an optical absorption technique, and (3) an ion chromatographic technique. The latter techinque is recommended for routine monitoring of retort water, although the relative advantages of each are discussed in the report. Total sulfur in retort gas is determined by combusting the gas in a continuously flowing system, whereupon the resulting sulfur dioxide is determined by $SO_2$ monitor. Individual sulfur species in retort gas including $H_2S$, COS, $SO_2$, $CS_2$, $CH_3CH_2SH$, and $CH_3CH_2SH$, are determined by gas (Over)

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|
| Fossil Fuels, Oil Shale pollution, chemical analysis, chromatographic analysis, flame photometry, gas analysis, spectroscopic analysis, volumetric analysis, water analysis | sulfate, thiosulfate, nitrate, thiocynate, total sulfur, sulfide, residue ammonia, hydrogen sulfide carbonyl sulfide, carbon disulfide, methyl mercaptan, ethyl mercaptan, pH | NTIS Terms:<br>97F--Fuel Conversion<br>97R--Energy, environmental studies<br>99A--Analytical Chemistry (Over) |

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