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ABSTRACT

During the last two years several methods of chemical analysis have been developed for oil shale wastewaters and gases. Emphasis has been placed on methods which are rapid, simple, and able to perform well under field conditions. Species which have been studied include total solutes, total N, total S, ammonium N, SO_4^- , NO_3^- , S_2O_3^- , SCN^- , SO_3^- , Cl^- , NO_2^- , and sulfide in wastewater; and total S, H_2S , COS , CH_3SH , CS_2 , $\text{CH}_3\text{CH}_2\text{SH}$, thiophene, propyl mercaptan, and butyl mercaptan in retort gas.

INTRODUCTION

Previous efforts to analyze retort waters and gases have demonstrated that the then-existing standard methods were often inadequate for retort waters and gases (Fox et al. 1978; Felix et al. 1977; Wallace 1981.) This situation caused an obvious problem, since pollution control systems cannot be designed and tested without a knowledge of stream composition, nor can emission regulations be promulgated rationally. For this reason we have been developing, over the last two years, a number of methods of chemical analysis for potential pollutants in oil shale waste streams. In this paper the main characteristics of these analyses will be summarized.

The objective of this work is to develop analytical methods which can be helpful in selecting, monitoring, and optimizing various types of control technologies for wastewaters and gases. In the case of wastewaters, present regulatory philosophy requires "zero discharge" of any contaminated water. The wastewater engineer is therefore concerned with conditioning retort wastewater streams for re-use within the plant and not for discharge. Consequently, the analytical methods developed must work well with colored, oily process waters such as are often found in an oil shale retort. On the other hand, detection limits required for such methods typically can be higher than for analytical methods used on discharged

waters. Additional requirements of analytical methods developed for this purpose are speed, ease of use, and the ability to operate in the field under less-than-ideal environmental conditions. The analyses described below are therefore designed to be used in field laboratories and to give feedback fast enough for the plant operator to optimize plant conditions.

Table 1 shows those species, selected for their importance in evaluating control technology, which have been investigated during the last two years. Methods have been developed for most species in this table with a few exceptions: an instrumental approach which was under investigation for measuring total N in water operated by combusting the sample in a resistance furnace and attempting to quantitate total N by measuring the yield of NO . However, early experiments indicated that different compounds yielded NO with different efficiencies, and for this reason efforts to develop a method for total N have been discontinued.

Methods for those species shown in parentheses in Table 1 are of an intermediate status. While it is likely that they can be measured by the ion chromatographic techniques developed during this study, their efficacy is not yet proven. For example, Na gives a clear peak during the ion chromatographic measurement of NH_4^+ , but the recovery, precision, potential interferences, and range of the Na measurement have not yet been measured. Similar comments apply to SO_3^- , NO_3^- , S_2O_3^- , and PO_4^- .

Table 1
ANALYTICAL METHODS UNDER STUDY

Water	Gas
total Solutes	total S
total N	H_2S
total S	COS , CH_3SH , CS_2
NH_4^+ (Na)	$\text{CH}_3\text{CH}_2\text{SH}$
SO_4^- , NO_3^- , S_2O_3^- , SCN^- (SO_3^- , Cl^- , NO_2^- , PO_4^-)	thiophene
Sulfide	PrSH, BuSH

However, for the remaining species, methods have been developed which have operated satisfactorily in the laboratory and in the field. Because of space limitations, the following text briefly summarizes the most important characteristics of these analyses. More detailed information will become available to the reader in reports which are presently being prepared.

Total Solute

During this same forum one year ago, John Wallace discussed the measurement of total solute content using the freezing point depression method, and the reader is referred to those proceedings for more details (Wallace et al. 1981). Suffice it to say that the freezing point depression indicates the total solute content of retort water, including volatile gases, in the concentration range 0.01 to 3 mol/l. It is suggested that this measurement can have the same utility that the total residue measurement has for wastewaters.

Sulfide

Although the literature describes numerous methods for measuring sulfide, many of these are not appropriate for retort waters. For example, the methylene blue colorimetric method and the iodometric titration method, both of which are commonly applied to less complex waters, are subject to interferences due to colored compounds or reducing agents and are, most likely, not suitable for retort waters (Wallace 1981). On the other hand, several authors have reported measuring sulfide in colored process waters by means of a Pb^{+} or Ag^{+} titration monitored by an AgS indicator electrode (Haas 1979; Swartz and Light 1970). This method was therefore evaluated for its applicability to retort wastewaters.

In the procedure tested, the sample is first diluted 1:1 with a basic ascorbic acid solution which acts as an anti-oxidant preservative and also converts the sulfide to $S^{=}$, the form reactive with the AgS electrode. This mixture is then titrated with $b(NO_3)_2$ while monitoring the response of the AgS electrode. The equivalence point is determined with a Gran's plot when a manual titration is carried out; however, a derivative endpoint may be more convenient for automated titrations.

This method was first tested in the laboratory and then in the field using actual retort waters for sulfide levels ≥ 1 mg/l. In this range no interferences could be observed when the method was challenged with Cl^{-} , SCN^{-} , $SO_4^{=}$, $S_2O_3^{=}$, carbonate, ammonia, or turbidity. Routine analyses performed under field conditions are reproducible to $\pm 3\%$ (1σ) although somewhat better results can be obtained, if required, by more careful application. The recovery of sulfide added to retort waters is 100% within experimental error.

Under field conditions this method has proven easy and reliable. One attractive feature is that all reagents are stable and no labile sulfide standards need to be prepared in the field.

Ammoniacal N in Water

Total ammoniacal N, referred to here as t-N, is typically one of the predominant species in retort water and is frequently of interest to pollution control engineers. For this reason t-N has been measured frequently but with mixed results. Some reports suggest that existing methods are adequate, especially if a distillation step is included. On the other hand, other investigators report erratic results, especially with the ammonia ion selective electrode (Wallace 1981). In our experience, the distillation techniques are too time consuming and cumbersome for field application while the ion selective electrode requires extraordinary patience and skill to achieve reliable results, even in the laboratory. The principal difficulty with the electrode technique is the occurrence of erratic shifts in the intercept of the calibration curve, although the slope normally stays constant. This shift is presumably caused by high ionic strength or high organic content of the retort waters. Due to these effects, results obtained in the field with the electrode were sometimes off by a factor of two; results could be obtained in the laboratory within a precision of $\pm 20\%$ only by recalibrating after every few samples and repeating the analyses whenever the calibration shifted.

Because of these experiences we began developing alternate methods for t-NH₃, and in the process investigated three different techniques. The first depends on the absorption of UV radiation by gaseous NH₃ which is evolved from a basic solution. The second method is a liquid chromatographic determination and the third method is a modification of the electrode method.

The UV absorption technique is carried out in a 150 ml, temperature controlled chamber fitted with quartz windows, as shown in Figure 1. Approximately 30 ml of sample is placed in the cell along with approximately 3 ml of 10 M NaOH. After the NH₃ has equilibrated between the headspace and liquid phase, the UV absorption of the gaseous NH₃ in the headspace is measured at 197 nm. For the most accuracy the wavelength is scanned across the sharp peak occurring at 197 nm and the background continuum is subtracted.

The modified electrode method is designed to avoid exposing the electrode to oily or briney waters, while at the same time taking advantage of the relatively stable slope. Before beginning a series of samples, the electrode is first calibrated with a series of NH₄Cl standards in d.i. water in order to ascertain the slope. Individual samples are then analyzed by first placing the electrode in a beaker containing 0.1 M NaOH and 5 mg/l of NH₄Cl. Micro-liter aliquots of the retort water are then added while monitoring the change in cell potential. The concentration is then determined by the shift in potential (rather than the absolute value of the potential) and the amount of retort water added.

The third technique employs a Dionex ion chromatograph to separate NH₄⁺ from other cations on a cation exchange resin. Eluant is .0075 mol/l HNO₃, and detection is by electrical conductivity. This technique also yields a clear peak of Na which presumably could be measured also, although we have not yet made efforts to confirm this supposition. K yields a peak following the NH₄⁺ peak and could become an interference if it was present in excess; however, this situation would appear to be highly unlikely in retort waters.

Table 2 shows a comparison of these three methods. Columns 3 and 4 in the table compare the results obtained with the UV method when the background continuum is subtracted from the peak height (column 3) with the values obtained when only a single wave-

length is monitored. As shown, the single-wavelength results are consistently higher, although the difference may not be important in every case.

The average difference shown in the fifth row is based on a larger series of samples which were analyzed by three different methods. The ion chromatographic method (IC) and the scanning UV method agree within experimental error; either technique is sufficiently accurate for measuring NH₃ in retort water. The larger difference shown for the electrode measurement is not due to a systematic error, but the poorer precision of the technique.

Table 2
COMPARATIVE AMMONIACAL NITROGEN
DETERMINATION (mg/l as NH₃)

Sample	IC	UV		Electrode (Std Addition)
		Scan	Singleλ	
GE0-17	2,200	2,149	2,300	2,191
Ω-9 (3125)	3,300	3,449	3,600	3,596
Tar Sands	55	50	102	68
Coal Gasi- fier Con- densate	4,000	4,199	4,200	4,127
Average Difference	0.00%	5%	14%	14%
N	12	12	12	13

In summary, each of these methods has advantages and disadvantages. The UV technique is relatively insensitive to oils and surfactants and requires a minimum of reagents and sample pretreatment. This method is therefore promising as the basis of a continuous field monitor. On the other hand, no such monitor is available commercially at the present time. In contrast, the modified electrode technique requires the least expensive equipment and the most labor. This method also exhibits the poorest precision. The ion chromatograph used for this analysis is commercially available but costs significantly more than an electrode system.

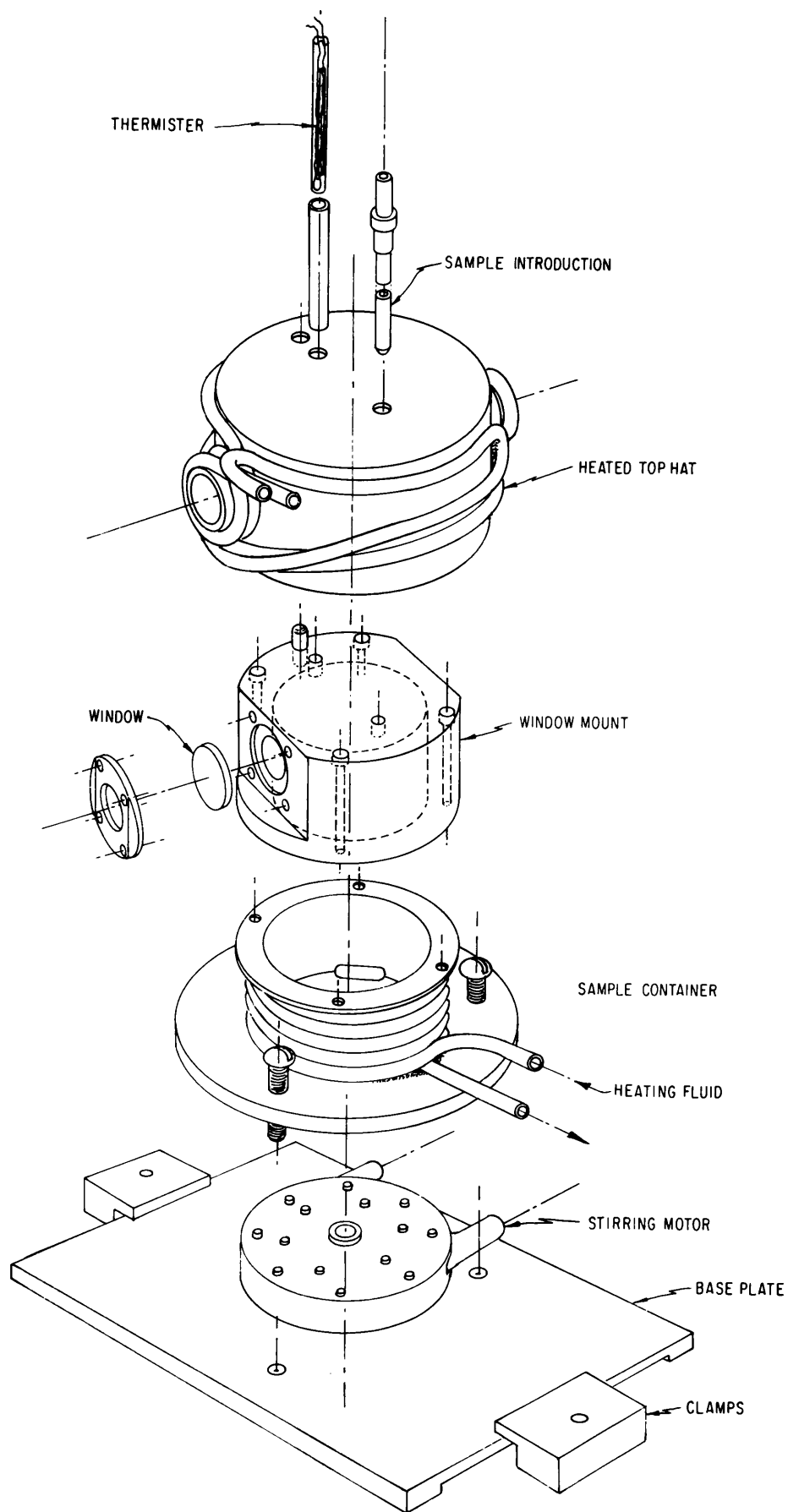


FIGURE 1 THERMOSTATED CELL FOR MEASURING NH_3 VAPOR OVER RETORT WATER

Anions in Retort Water

In addition to the measurement of $t\text{-NH}_3$, ion chromatography has proven to be a useful technique for the measurement of anions in retort waters. Four separate protocols have been developed for the major and minor anions (except $\text{CO}_3^{2-}/\text{HCO}_3^-$) in retort wastewaters.

All analyses have been performed on a Dionex (Sunnyvale, CA) Model 10 ion chromatograph equipped with an electrical conductivity detector. Columns selected for these analyses are the Dionex "fast run" pre-columns, and a resin-based anion suppressor column.

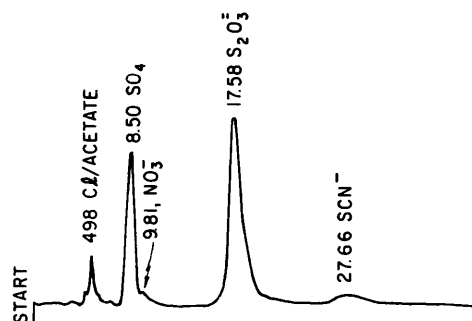
The first analysis is designed to measure only $\text{S}_2\text{O}_3^{2-}$ and SCN^- , which are the slowest eluting peaks observed in retort waters. This analysis is accomplished with 2 pre-columns using an eluent of .007 mol/l Na_2CO_3 + .0005 mol/l SCN^- . Detectability of these species under these conditions is approximately 3 mg/l, and the analysis is completed in approximately 25 minutes. While this protocol is best for $\text{S}_2\text{O}_3^{2-}$ and SCN^- , earlier eluting compounds such as SO_4^{2-} and SO_3^{2-} are not adequately separated.

The major anions SO_4^{2-} , NO_3^- , SCN^- , and $\text{S}_2\text{O}_3^{2-}$ can be measured in a single run by combining two pre-columns with an analytical column. At the start of the analysis the two pre-columns are temporarily switched in line in order to retain the SCN^- and $\text{S}_2\text{O}_3^{2-}$, while SO_4^{2-} and NO_3^- , as well as any earlier eluting compounds, are allowed to proceed to the analytical column where they are separated and detected. The pre-columns are then switched back in line as the analytical column is switched out of line, thereby allowing $\text{S}_2\text{O}_3^{2-}$ and SCN^- to proceed to the detector. For this analysis .007 mol/l Na_2CO_3 is the eluent.

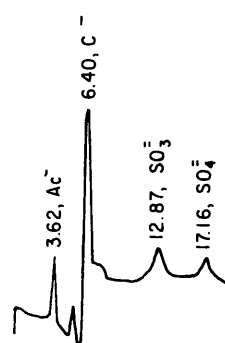
The chromatogram shown in Figure 2A illustrates several features of this analysis as applied to retort water. (The number shown by each peak indicates retention time, not concentration.) As shown in this figure, under these conditions SCN^- is a rather diffuse peak. For this reason, SCN^- is not reported at concentrations below 10 mg/l. Also, compounds eluting before SO_4^{2-} are not adequately separated to permit identification. For example, the first peak in Figure 2A could be either Cl^- or acetate. As is normally the case with retort waters, NO_3^- does not give a detectable peak. However, NO_3^- can be readily ob-

served, if added to the sample as a separate peak following SO_4^{2-} . Other ions such as SO_3^{2-} and HPO_4^{2-} elute, albeit incompletely resolved, between Cl^- and SO_4^{2-} , and a peak in this region alerts the analyst to the possible need for a more detailed separation.

The third ion chromatographic protocol uses a weaker eluent (.003 mol/l Na_2CO_3) in order to better separate the early first peaks such as Cl^- , acetate, NO_2^- , SO_3^{2-} , and SO_4^{2-} . SCN^- and $\text{S}_2\text{O}_3^{2-}$ are trapped on a pre-column and periodically flushed to waste. An example of this separation is shown in Figure 2B. As suggested by this figure, it is nevertheless difficult to quantitate Cl^- or earlier peaks because of baseline shifts at the beginning of the chromatogram.



A. INFLUENT TO STEAM STRIPPER. ELUENT = 7 mM Na_2CO_3



B. REFLUX SAMPLE FROM STEAM STRIPPER. SO_4^{2-} AND SCN^- ARE NOT SHOWN BUT WOULD ELUTE LATER. ELUENT = 3 mM Na_2CO_3

FIGURE 2. ION CHROMATOGRAMS OF RETORT WASTEWATER

The fourth analysis is for total S. Retort water is oxidized with H₂O₂ to a fixed Eh, and then analyzed for SO₄⁼. Experiments in our laboratory have shown that this procedure successfully converts the various forms of S to SO₄⁼.

Total Sulfur in Retort Gas

Total S in retort gas is of interest for two reasons: First, it serves as a quality control function in that the measurements of individual S gases should sum to the total S measurement. Second, total S removal is the "bottom line" in evaluating a S pollution control system, since the remaining S gas would be burned and converted to SO₂ before emission.

The measurement of total S is most easily accomplished by converting the various chemical forms of S to a single species in a quantitative manner. The total S analyzer developed for this study accomplishes this end by metering a known volume of retort gas into an air/methane flame, where the various S species are converted, within experimental error, to SO₂. The SO₂ is then measured using various stack gas monitors which are commercially available.

Table 3 shows the response of this analyzer to various S gases prepared as artificial standards in both H₂ and N₂. As can be seen, the response is constant within experimental error.

Table 3
RESPONSE OF TOTAL SULFUR ANALYZER TO
VARIOUS SULFUR GASES

S-species	Range (ppmv)	Response (%)
SO ₂	--	100
H ₂ S	280-34,000	100±4
CH ₃ SH	980-4,000	98-102
Thiophene	1,100-32,000	97-101
COS	3,200-26,000	97-100
CS ₂	2,900-7,250	95-98

A prototype of the total S analyzer has been field tested for a two-week period at the 150-ton retort operated by the Laramie Energy Technology Center (LETC). Results for the total S measurement were within the range calculated from the measure-

ment of individual S species. However, additional work is required on this system to permit the introduction of hot, saturated, retort gas and to minimize operator labor requirements.

Sulfur Species in Retort Gas

Although gas chromatography with a flame photometric detector (GC/FPD) had been used for many years to determine various S gases, it was not clear how this technique could best be applied to retort gas. Which columns, if any, could separate the S compounds found in retort gas without being damaged by the accompanying moisture and oils? Hydrocarbons found in retort gas were known to quench the signal from the FPD. Would such quenching degrade the quality of the results?

The effect of hydrocarbon quenching on a Baseline (Lyons, CO) single-flame photometric detector used in the normal mode is shown in Figure 3. To relate this to retort gas consider a 10 µl injection volume of gas containing 5,000 ppmv H₂S and 1% co-eluting ethane. According to the figure, the response of the detector would be approximately 10% too low. Additional experiments have shown that quenching effects can be minimized by reversing the introduction of H₂ and air to the FPD so that air is introduced concentric to the outer layer of H₂. Quenching effects are also kept within acceptable levels by using peak height instead of peak area and by minimizing the injection volume.

Of the various packed columns which were evaluated, two have been selected for routine use based on their insensitivity to water and their ability to separate the major S gases suspected to be in retort gas. These columns are the Carbopack BHT-100 from Supelco for H₂S, COS, CH₃SH, CH₃CH₂SH, and CS₂, and a Porapak QS, acetone washed, for H₂S. Figure 4 shows a chromatogram obtained with gas produced at the 150-ton retort located at the LETC. Two injections were used in order to stay within the dynamic range of the flame photometric detector, the first injection of 1 µl H₂S, and the second injection of 100 µl for the minor S gases.

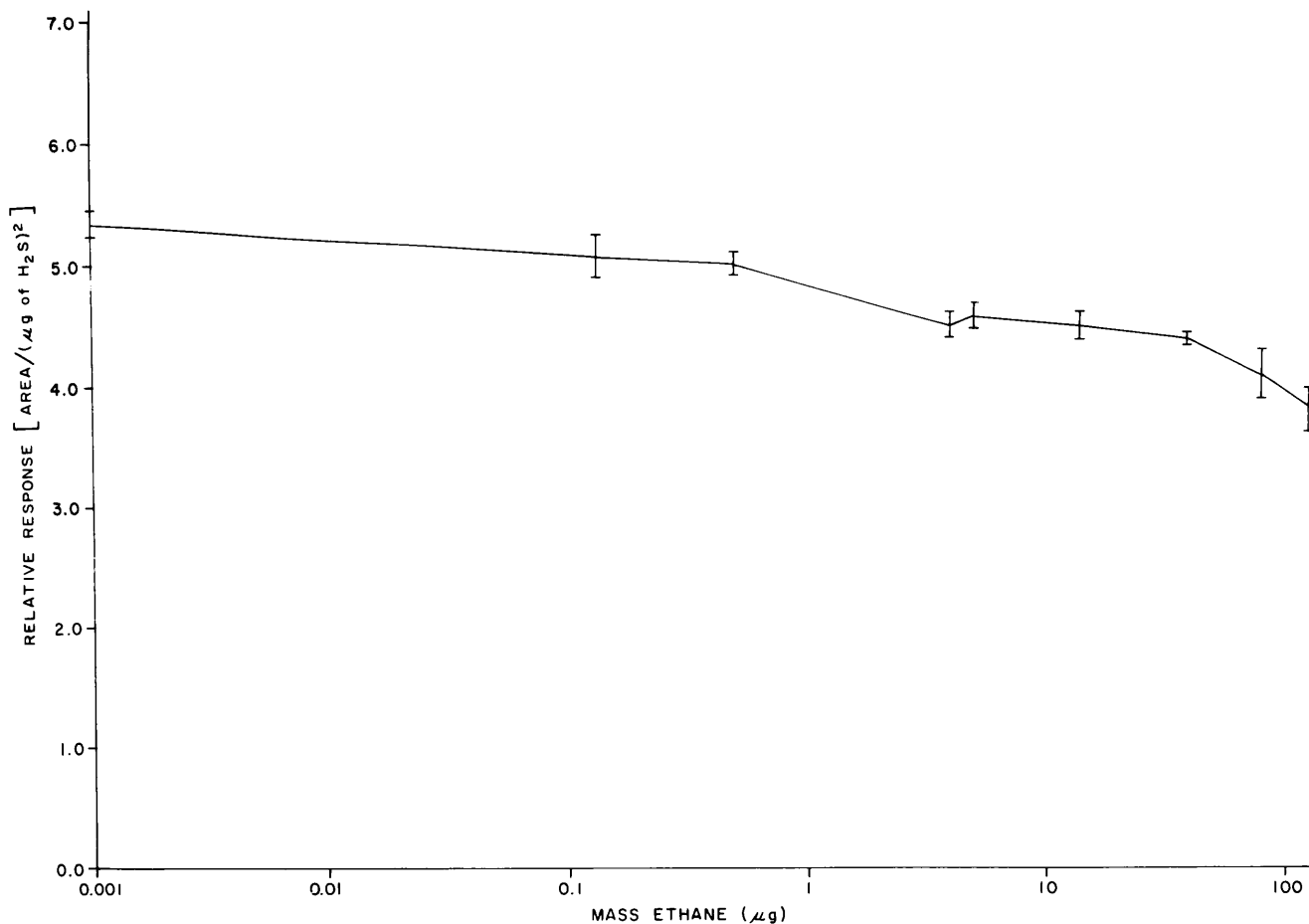


FIGURE 3 SUPPRESSION OF FPD RESPONSE BY CO-ELUTING ETHANE

As shown in Figure 4, the Carbopak BHT-100 column is adequate for separating H_2S and some of the minor S gases. This conclusion has also been supported by injecting a variety of other S gases in order to ascertain their relative elution times. In conjunction with an FPD being operated under the conditions discussed in the previous paragraph, packed column gas chromatography is thus an acceptable method for measuring a limited number of S species in retort gas.

ACKNOWLEDGEMENT

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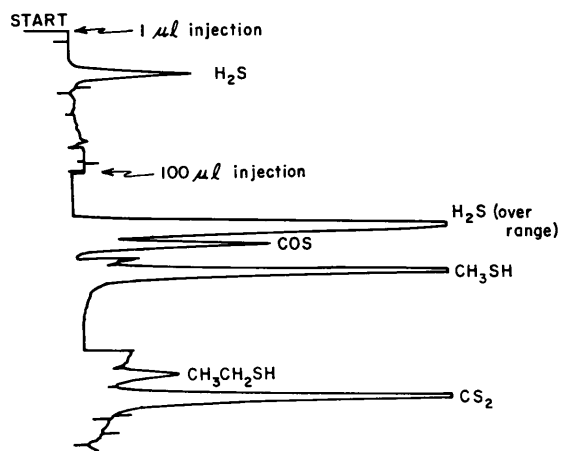


FIGURE 4. GAS CHROMATOGRAM OF RETORT GAS

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