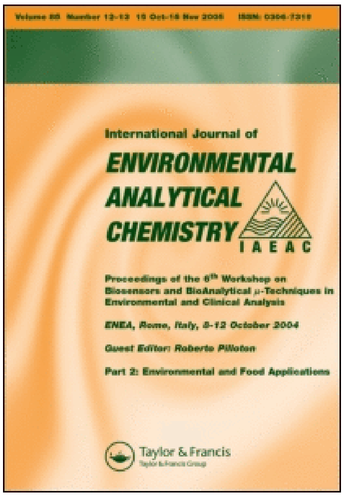

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ARSENIC IN NATURAL GAS: ANALYSIS AND CHARACTERIZATION OF PIPELINE SOLIDS BY ^{1}H NMR AND OTHER METHODS

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Natural gas from the Abo gas field in New Mexico is known to contain arsenic in the form of tertiary alkylarsines. Deposition of alkylarsine sulfides near the pressure regulation equipment in the transmission lines may cause serious operational problems. ^{1}H NMR spectra of $CDCl_3$ solutions of the pure compounds, trimethylarsine sulfide (TMAS), dimethylethylarsine sulfide (DMEAS) and methyldiethylarsine sulfide (MDEAS) were measured.

The signlet resonance of the CH_3-group bonded to As is well separated in the three compounds: TMAS (1.83 ppm), DMEAS (1.74 ppm) and MDEAS (1.66 ppm). Based on this, a method for the analysis of the pipeline solids has been developed. Analysis of two samples indicate that the pipeline solids have the following composition, DMEAS (42.8 - 46.0%), TMAS (35.4 - 36.3%), MDEAS (4.7 - 10.9%). The identification of the arsenic compounds obtained by the ^{1}H NMR method has been confirmed by GC-MS analysis of the pipeline solids. A study of the reaction, in the gas phase, between TMA and sulfur-containing compounds (H_2S or CH_3SH) in the presence of potentially catalytic materials indicates that the presence of H_2O and a metal (Fe or Cr) is necessary for the formation of TMAS by the reaction of TMA with H_2S.

KEY WORDS: Arsenic, natural gas, ^{1}H NMR, pipeline

INTRODUCTION

The presence of arsenic in natural gas from certain gas fields is a comparatively recent discovery. In 1987, personnel of a very large gas distribution utility in California first noticed the formation of tan or white deposits which were plugging up the pilot regulator orifices in one of their major transmission lines.[1] Similar deposits were later found further down the distribution system at or near pressure regulation equipment where pressure changes of 100 psi or more were involved. At this time (early 1988), the arsenic compounds present in the natural gas had not been identified.

Analysis of the pipe line solids indicated that they were organic sulfur-containing arsenic compounds. Later these solids were identified as mixtures of trialkylarsine sulfides, primarily, trimethylarsine sulfide.[1,2] In addition to the health concerns arising from the bad reputation of arsenic compounds, the formation of these deposits gave rise to operational problems. These deposits caused the pressure regulation equipment to malfunction which resulted in an outage or overpressurization. As the result of an extensive investigation by the utility company, the contaminated gas was traced to the Abo gas field in Southeastern New Mexico. In 1989, we undertook an investigation to develop methods of analysis for the arsenic compounds present in natural gas from the Abo gas field. Attempts were also made to develop alternative procedures for the removal of arsenic. In an earlier publication[2], we reported that arsenic in natural gas is present in the form of trialkylarsines, R_3As, R = CH_3, C_2H_5. Trimethylarsine $(CH_3)_3As$ was found to be the principal species, accounting for between 55 - 80% of the total arsenic. Analytical procedures for the determination of total arsenic by extraction and oxidation of the organoarsines by conc. HNO_3[2] or by a saturated solution potassium peroxydisulfate[3] followed by hydride generation - d. c. helium plasma emission spectrometry (HG-DCHPES) were described. The problems relating to the depletion, with time, of arsenic in natural gas samples stored in nickel- or chromium-containing steel cylinders were also addressed. Of considerable interest, also, are the development of reliable methods for the analysis of the pipeline solids and the obtaining of some information on the mechanism of their formation.

Preliminary experiments indicated that these solids were almost quantitatively soluble in methylene chloride. Recrystallization from boiling methanol yielded colorless, well defined crystals which gave excellent ^1H NMR spectra. In this paper we describe a procedure, based on ^1H NMR measurements, which can be used to quantitatively characterize the pipeline solids. The pure trialkylarsine sulfides which are most likely to be present in the pipeline solids were synthesized in order to provide calibration data.

Both from the pragmatic and scientific points of view it is important to understand the mechanism(s) by which the trialkylarsine sulfides are formed in the pipelines. It is known, based on our own experience and that of many other investigators, that arsenic has a strong affinity for sulfur.[4] Hydrogen sulfide which is usually present in natural gas is the component most likely to react with arsines to form arsine sulfides. However, H_2S is essentially quantitatively removed during processing. Other sulfur-containing compounds which may be originally present (or added as odorants) are thiols, thioethers, thiophene and disulfides (from thiols). The reaction of alkylarsines, primarily trimethylarsine, with some of the sulfur-containing compounds has been studied under variety of experimental conditions and the results are reported. Also, it is well-known in the gas industry that pipeline residues contain pyrophoric iron sulfides. These residues (lateral pig residues) which are removed during the pigging of gas pipelines are presumed to be formed by the reaction between the iron in the walls of the pipelines and H_2S. It is very likely that these residues may be a good source of reactive sulfur. The results of some experiments on the reaction between trimethylarsine and H_2S in the presence of the lateral pig residues are also reported in this paper.

MATERIALS AND METHODS

Reagents

Trimethylarsine (TMA) used in this study was synthesized and donated by Mr. Jinggao Liu of the Department of Chemistry, Texas A & M University. Additional quantities of reagent grade $(CH_3)_3As$ were purchased from the Strem Chemical Company. Dimethylarsinic acid $(CH_3)_2As(O)(OH)$, (Aldrich) and arsenic trichloride, $AsCl_3$, (Cerac) were of the reagent grade. Methanearsonic acid $(CH_3)As(O)(OH)_2$, was furnished by Vineland Chemical Company.

Preparation of trialkylarsine sulfides

Methods described in the literature, with minor modifications, were utilized for the syntheses and purification of the arsine sulfides used in the study. In the preparation of trimethylarsine sulfide (TMAS) and triethylarsine sulfide (TEAS), the arsine (in our case only TEA had to be prepared since TMA was available) was prepared by condensation of $AsCl_3$ with the appropriate Grignard reagent:

$$AsCl_3 + 3\ C_2H_5MgBr \longrightarrow (C_2H_5)_3As + 3\ MgBrCl$$

Following acid hydrolysis, the layers were separated and the ether layers were dried over sodium sulfate and the ether was removed by distillation.

Trimethylarsine sulfide was prepared by the reaction between TMA (0.20 mole) in benzene (20.0 mL) with elemental sulfur (0.25 mole) in a sealed, thick-walled glass tube.[5] The tube was kept in a steel pipe for safety and slowly heated to 70°C (3 h) and kept at this temperature for 2 days. On cooling, white crystals separated from the mother liquor. The glass tube was broken and the crystals collected and recrystallized from absolute ethanol. A yield of 90% was obtained.

Triethylarsine sulfide was prepared by refluxing TEA (0.40 mole) with elemental sulfur (0.50 mole) in absolute ethanol to obtain TEAS as a white solid.

Dimethylchloroarsine $(CH_3)_2AsCl$, which is a starting material for the preparation of dimethylethylarsine sulfide (DMEAS) was prepared according to the method of Laughlin.[6] Phosphorus trichloride, PCl_3 (3 moles) in a 2 L separatory funnel equipped with three necks was cooled in an ice bath. Dimethylarsinic acid was very slowly added, taking care to maintain the temperature in the 25–28°C range with vigorous stirring. After completing the addition, the stirring was continued until the mixture cooled to a temperature of 10°C. The mixture was hydrolyzed by the very slow addition of 200 ml of concentrated HCl, producing two layers. $(CH_3)_2AsCl$ was recovered in the bottom layer as a yellow oil, dried and distilled (80% yield). In a procedure very similar to the one used in the preparation of TEAS, the haloarsine $(CH_3)_2AsCl$ was first reacted with C_2H_5MgBr to obtain dimethylethyl arsine (DMEA)

$$(CH_3)_2AsCl + C_2H_5MgBr \longrightarrow (CH_3)_2As(C_2H_5) + MgBrCl$$

Refluxing DMEA (0.25 mole) with elemental sulfur (0.30 mole) in absolute ethanol gave dimethylethylarsine sulfide (DMEAS), $(CH_3)_2As(S)C_2H_5$ as a white solid. Methyldiethylarsine sulfide (MDAS), $CH_3As(S)(C_2H_5)_2$ was prepared starting with methyldiiodoarsine, CH_3AsI_2. Methyldiiodoarsine was prepared according to the method of Claeys.[7] In a 2 L separatory funnel methane arsonic acid ($CH_3AsO(OH)_2$) (1 mol) and KI (2 mole) were dissolved in 350 mL of water and 85 mL of concentrated HCl was added. The mixture was stirred vigorously and SO_2 was passed through the mixture for 4 hours. The reaction produced an amorphous yellow precipitate which melted by the heat produced by the reaction and separated as a yellow oil constituting the bottom layer. Another 85 mL of HCI was added to complete the reaction:

$$CH_3AsO(OH)_2 + SO_2 + 2\ HI \longrightarrow CH_3AsI_2 + H_2SO_4 + H_2O$$

The yellow oil was recovered and extracted with dry ethyl ether, which upon evaporation yielded yellow acicular crystals. Methyldiethylarsine sulfide (MDEAS) was prepared starting with CH_3AsI_2 by a procedure identical to the one used in the preparation of

$(C_2H_5)_3As(S)$. Each of the arsine sulfides synthesized was purified by repeated recrystallization from absolute ethanol to a constant melting point. The melting points obtained are TMAS, $(CH_3)_3AsS$, 183.0°C; DMEAS $(CH_3)_2As(S)(C_2H_5)$, 120°C; MDEAS, $CH_3As(S)(C_2H_5)_2$, 97°C; TEAS $(C_2H_5)_3AsS$, 123°C. The IR spectra of the arsine sulfides were measured and the presence of the intense and highly characteristic As = S band in the region of 470 cm^{-1} was confirmed.

The following sulfur compounds: hydrogen sulfide, H_2S, methyl mercaptan, CH_3SH, ethyl mercaptan, C_2H_5SH, dimethyl sulfide $(CH_3)_2S$, dimethyl disulfide, $(CH_3)_2S_2$, diethyl disulfide, $(C_2H_5)_2S_2$, all of reagent grade (Aldrich Chemical Company) were used without further purification.

Lateral pig residue (from Pecan Island, Louisiana, furnished by Columbia Gulf Transmission Company) and high purity metallic chromium and nickel were studied as catalysts in the gas phase reaction.

The gas phase reactions were studied in an all-glass manifold constructed in the Texas A&M University, Department of Chemistry glass shop. The manifold (Figure 1) consisted of an 18″ long, 2″ diameter glass pipe with three 2-liter round bottom flasks connected at the top, 9″ apart from one-another. Each flask, equipped with a cold finger, was used as a separate reservoir for each of the gases used in a reaction. At the bottom, a round bottom flask (0.5 L or 1.0 L capacity) was connected to the center of the glass pipe and served as the reaction chamber. All joints, and stopcocks were of the high vacuum O-ring type constructed with appropriate gasket material. At one end of the manifold a stopcock was placed to be used as a port to charge the system with different gases. At the other end the system was connected to a vacuum pump via two traps the first cooled in liquid nitrogen, the second in dry-ice/isopropanol.

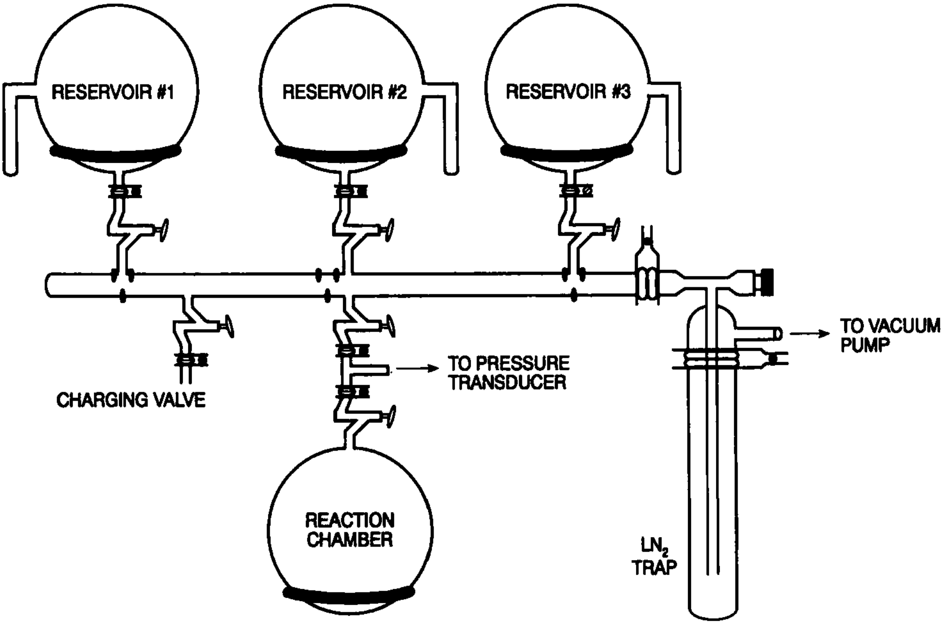

Figure 1 Vacuum manifold for study of gas-phase reactions.

Table 1 Summary of ^{1}H NMR spectral data for trialkylarsine sulfides[a,b]

	Chemical Shift, δ (ppm)		
	– CH_3 (bonded to As) Singlet	*– CH_3 (terminal) triplet*	*– CH_2 – quartet*
$(H_3C)_3AsS$	1.83	–	–
$(H_3C)_2As(S)C_2H_5$	1.74	1.33	2.07
$H_3CAs(S)(C_2H_5)_2$	1.66	1.32	2.03
$(C_2H_5)_3AsS$	–	1.30	2.00

[a] Solvent: $CDCl_3$
[b] All chemical shifts relative to trimethylsilane

Instruments

All the ^{1}H NMR spectra were obtained using a 200 MHz Varian XL200 spectrometer at room temperature. The gain of the instrument was adjusted to 16 arbitrary units (a.u.), the vertical scale was adjusted accordingly and the integration scale was fixed at 500 a.u.

A Hewlett Packard GC-MS Model HP 5995 equipped with a data processor, MS ChemStation Model 59970, was used for the separation and identification of the compounds. The instrument was equipped with a DB-5 column (5% phenyl- 95% methyl polysiloxane). The following temperature program was employed, 5 min at 70°C, heating rate of 15°C/min. and held at 200°C for 5 minutes. The injector port, ion source, transfer line and mass analyzer were each maintained at 200°C. The scanning rate was maintained at 0.92 scans/sec.

The infrared spectra were taken with an IBM IR/44 Version 1.0 F spectrometer. The melting points were measured on a Büchi SMP-2 Melting Point apparatus.

RESULTS AND DISCUSSION

^{1}H NMR spectra of the pure arsine sulfides

The ^{1}H NMR spectra of four trialkylarsine sulfides which may form in natural gas pipeline systems were measured in their $CDCl_3$ solutions and the results are summarized in Table 1. From the analytical point of view, a very useful feature of the spectra are the resonances of the methyl groups bonded to arsenic which are very intense and narrow. With the sequential substitution of the methyl groups in $(CH_3)_3AsS$ with two ethyl groups there is a significant movement of the methyl singlet peaks so that they are well separated (Figure 2). The ethyl resonances (CH_2 bonded to arsenic and terminal CH_3 in $AsCH_2CH_3$) badly overlap in the three compounds containing ethyl groups(s) and do not appear to be useful for the analysis of these compounds in their mixtures.

Calibration standards for analysis of trialkylarsine sulfides

As discussed in the previous section, the measurement of the intensity of the methyl singlet resonance appears to be ideally suited for the analysis of the trialkylarsine sulfides. In order to evaluate this possibility, a series of calibration standards was prepared from authentic samples of $(CH_3)_3AsS$, $(CH_3)_2As(S)(C_2H_5)$ or $CH_3As(S)(C_2H_5)_2$. The area of the methyl singlet peak at each concentration was measured. It should be

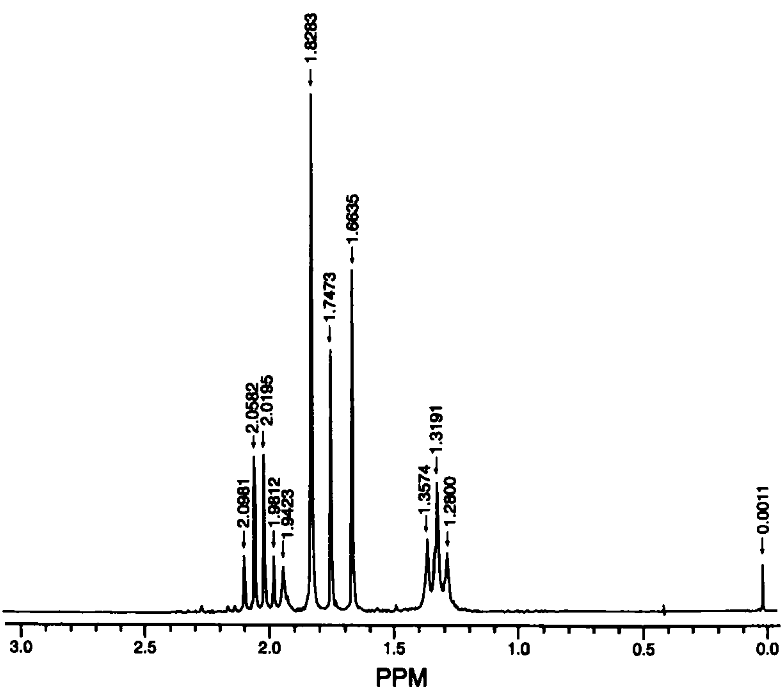

Figure 2 ^{1}H NMR spectra of the pure arsine sulfides.

mentioned that the methyl resonance is shifted slightly downfield with increasing concentration in the case of each compound: $(CH_3)_3AsS$, 1.820 ppm (0.010 M), 1.835 ppm (0.50 M); $(CH_3)_2As(S)C_2H_5$, 1.741 ppm (0.05 M), 1.730 ppm (0.13 M); $CH_3As(S)(C_2H_5)_2$, 1.661 ppm (0.10 M), 1.668 ppm (0.50 M). The chemical shift value (methyl singlet) for each substance given in Table 1 represents the average for the specified concentration range.

The linear least square parameters for the plot of peak area for the methyl singlet vs concentration for each arsine sulfide are given in Table 2. Also included are data for $(C_2H_5)_3AsS$ of the peak area measurements made at ~1.30 ppm (terminal CH_3). From the data given in Table 2 it can be seen that there exists an excellent linear correlation between peak area and concentration for all of these compounds. In order to further confirm the viability of this analytical procedure, a series of mixed solutions containing known concentrations of the three arsine sulfides was analyzed. The analytical results

Table 2 Linear regression parameters in calibrations for ^{1}H NMR analysis of arsine sulfides.

Compound	*Slope (a. u./mole L^{-1})*	*y-intercept (a.u.)*	*x-intercept (M)*	*correlation coefficient*
TMAS	319.2	−0.32	0.001	0.9988
DMEAS	223.2	−0.99	0.004	0.9934
MDEAS	86.3	0.49	−0.005	0.9998
TEAS	280.2	−2.8	0.01	0.9983

Table 3 Analysis of mixtures of arsine sulfides by ^{1}H NMR.

Sample	*[TMAS]$_M$*		*[DMEAS]$_M$*		*[MDEAS]$_M$*	
	True	*Found*	*True*	*Found*	*True*	*Found*
M-1	0.13	0.13	0.042	0.038	–	–
M-2	0.25	0.22	–	–	0.25	0.21
M-3	0.25	0.23	–	–	–	–
M-4	0.10	0.09	0.034	0.034	0.10	0.09
M-5	0.17	0.13	–	–	0.17	0.17
M-6	0.10	0.09	0.023	0.024	0.10	0.09
M-7	–	–	0.042	0.045	0.13	0.08
M-8	–	–	0.042	0.042	–	–
M-9	–	–	0.034	0.033	0.10	0.09
M-10	–	–	–	–	0.25	0.25

Composition of samples:

M-1	TMAS + DMEAS
M-2	TMAS + MDEAS
M-3	TMAS + TEAS
M-4	TMAS + DMEAS + MDEAS
M-5	TMAS + MDEAS + TEAS
M-6	TMAS + DMEAS + MDEAS + TEAS
M-7	DMEAS + MDEAS
M-8	DMEAS + TEAS
M-9	DMEAS + MDEAS + TEAS
M-10	MDEAS + TEAS

given in Table 3 show good agreement between the calculated and measured concentrations in the solutions. These results confirm the expectation that the arsine sulfides do not interfere with one another in the analysis by this method.

Analysis of the pipeline solids

Two samples (ID#'s, AS90B and AS92B) of the arsenic-containing white solids collected from two locations in the gas distribution system were furnished by the utility company in Southern California. The appearance of the samples indicated the presence of extraneous debris. A weighed amount of each sample was dissolved in a known volume of $CDCl_3$ (25 mL for AS90B and 10 mL for AS92B) and filtered through a membrane filter. Aliquots of these solutions were further diluted (x10) and ^{1}H NMR measurements were made. The ^{1}H NMR spectrum of one of the samples (AS92B) is given in Figure 3. Comparison of Figures 2 and 3 clearly indicates the presence of $(CH_3)_3AsS$, $(CH_3)_2As(S)(C_2H_5)$ and $(CH_3)As(S)(C_2H_5)_2$ in the sample. The areas under the peaks at ~ 1.83, 1.74 and 1.66 ppm were measured. The concentration of each arsine sulfide was calculated by appropriate interpolation of the peak areas in the calibration parameters given in Table 2. The analytical information on the pipeline solids obtained by ^{1}H NMR measurements is given in Table 4. In both the samples DMEAS and TMAS, in that order, are the major components with MDEAS being present in smaller amounts. These results are in general agreement with our findings reported earlier.[2] In that study, gas samples at the well-head were extracted into concentrated HNO_3 and analyzed by HG-DCHPES without mineralizing the samples prior to analysis. Under these conditions, the integrity of the C-As bonds is maintained. The organo arsines produced

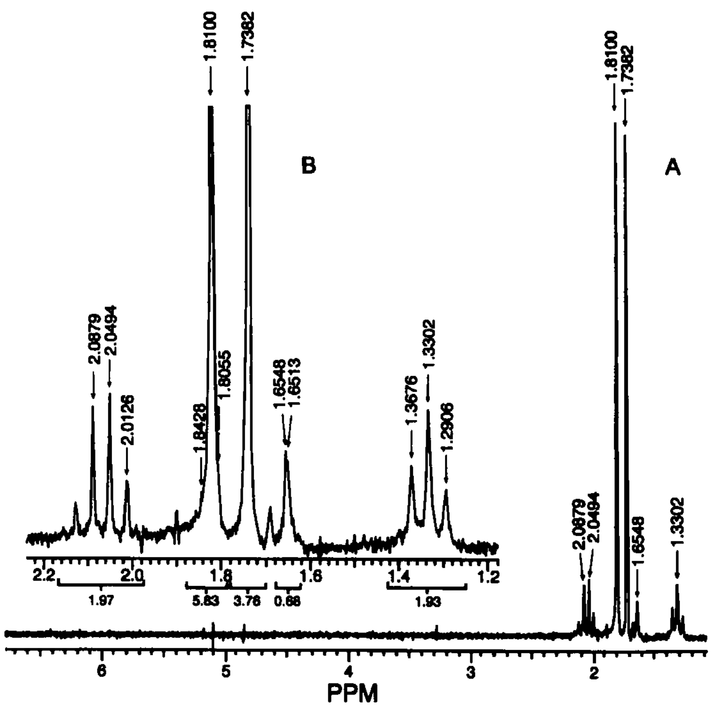

Figure 3 ^1H NMR spectrum of pipeline solid (AS92B).

by the borohydride reduction were condensed in a liquid N_2 trap and analyzed by fractional volatilization into the d.c. helium plasma. Using this technique, TMA was the only arsenic compound identified and accounted for approximately 50% of the total arsenic present. The methyl ethylarsines could not be analyzed by this procedure because of their higher boiling points. It is also likely that the relative concentrations of the organo arsines may vary depending on the source of the natural gas. This may explain the higher TMA/DMEA ratios found in the natural gas samples analyzed by low temperature GC-MS[2] data compared to the TMAS/DMEAS ratios in the pipeline solids measured in the present study.

Table 4 Analysis of Pipeline Solids by ^1H NMR

Sample	*AS90B*	*AS92B*
wt. of sample	2.045 g	0.76802 g
Peak area[a] (1.83 ppm)	5.83	5.62
TMAS, M	1.92×10^{-2}	1.86×10^{-2}
% TMAS in original sample	35.4	36.3
Peak area (1.74 ppm)	3.76	3.83
DMEAS, M	2.13×10^{-2}	2.16×10^{-2}
% DMEAS in original sample	42.8	46.0
Peak area (1.66 ppm)	0.68	0.90
MDEAS, M	2.17×10^{-3}	4.72×10^{-3}
% MDEAS in original sample	4.72	10.9
Total arsine sulfides, % of original sample	**83.0**	**93.2**

[a] Peak areas in arbitrary units

Table 5 Comparison of total arsenic concentrations of pipeline solids calculated from ^1H NMR measurements and the experimental values.

Sample	*1H NMR*	*Total arsenic concentration %* *HG-DCHPES*	*GFAAS*
AS90B	38.8	37.4 (± 0.5)	35.5
AS92B	43.1	40.7 (± 1.6)	38.5

The arsine sulfides comprise of 83% of the sample AS90B and 93% of the sample AS92B. The remainder in each sample is likely to be made up of one or more of the following components:

- Arsenic-containing organics not detected by this method, e.g., TEAS.
- Non-arsenic containing organics
- Elemental sulfur (evidence for its presence is discussed in a later section)
- Debris (paint chips, etc.)

Based on stoichiometric considerations, the total arsenic concentration of each sample is easily calculated from the arsine sulfide concentrations. The samples were also analyzed for total arsenic by HG-DCHPES following mineralization with a saturated solution of potassium peroxydisulfate.[3] In addition, results of analyses for total arsenic by graphite furnace atomic absorption spectrometry carried out by the California utility company were furnished to us. The total arsenic concentrations from these three sources are given in Table 5. It is clear that the agreement between the calculated values and the experimental values, in particular, the HG-DCHPES value, is excellent. This agreement confirms the validity of ^1H NMR method for the analysis of the pipeline solids.

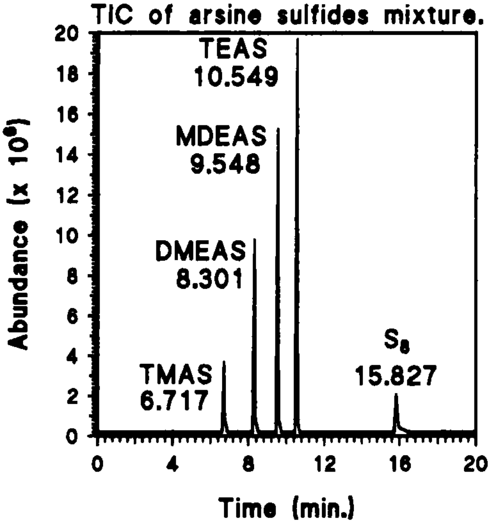

Figure 4 Total ion chromatogram (TIC) of a mixture of arsine sulfides.

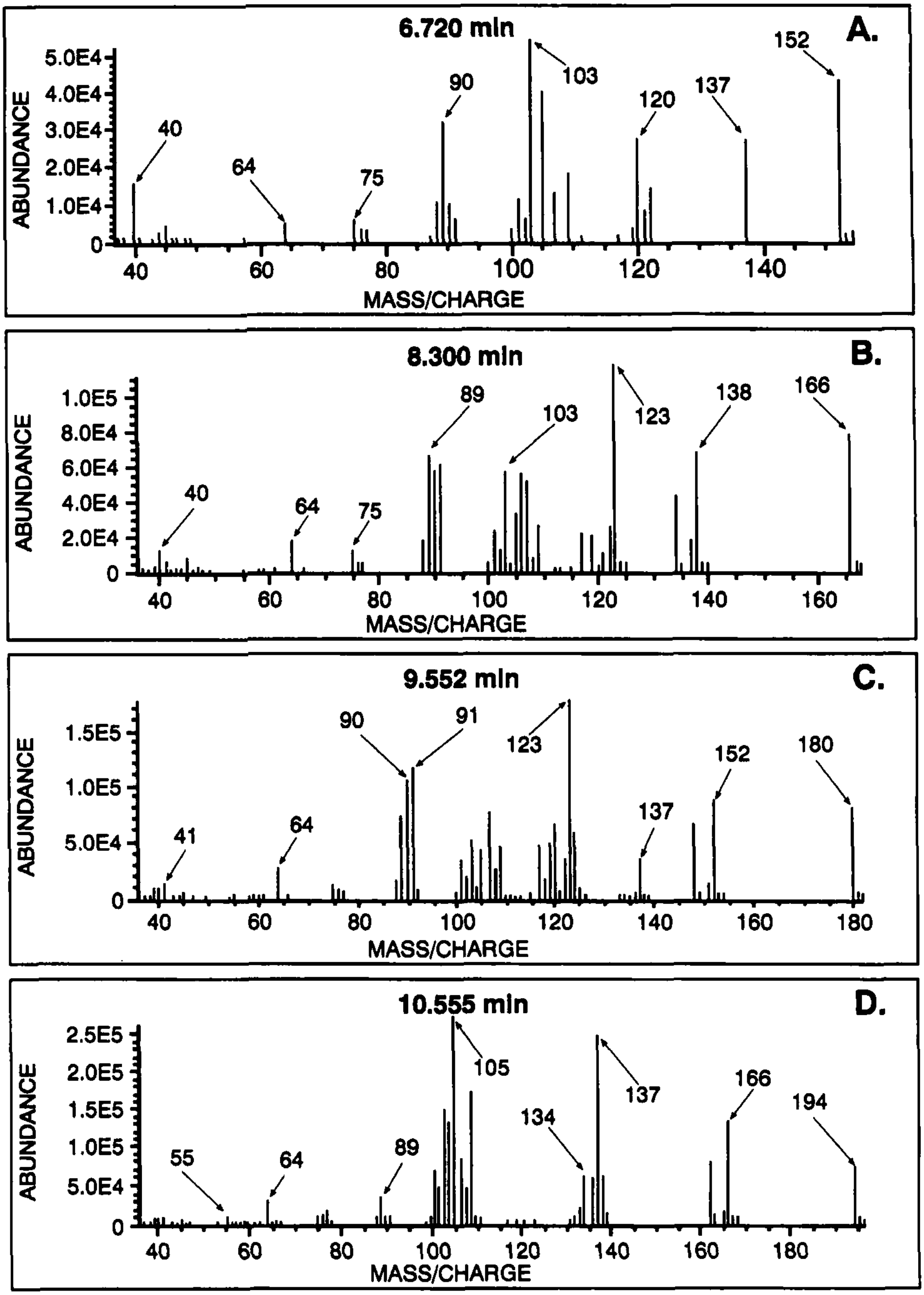

Figure 5 Mass spectra of mixture of arsine sulfides: A, TMAS; B, DMEAS; C, MEAS; D, TEAS

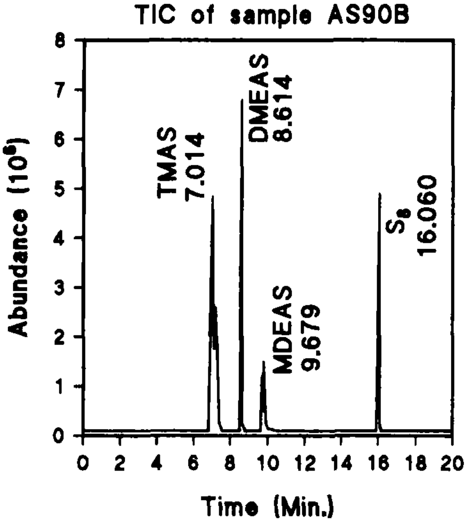

Figure 6 TIC of pipeline solid (AS90B)

GC-MS measurements

In order to independently confirm the identification (^{1}H NMR) of the R_3AsS compounds in the pipeline solids, a GC-MS study was undertaken. The total ion chromatogram of a mixture of authentic samples of the four arsine sulfides, each at a concentration of 0.0125 M is given in Figure 4. It is evident that the compounds are well separated on the DB-5 column. The mass spectra at the indicated retention times are also given in Figure 5. The compounds TMAS, DMEAS, MDEAS, TEAS are desorbed from the column in that order and were identified by the presence of the molecular ion peaks at 152, 166, 180 and 194 mass units, respectively. The peak at 256 (15.83 min.) is apparently due to elemental sulfur (S_8) which tends to be a persistent impurity in these preparations.

Since the GC-MS behavior of AS90B and AS92B were very similar, only that of AS90B will be described. The analyte solution contained 0.0825 g sample per mL and 1µL was injected. The TIC and the mass spectra at the indicated retention times are given in Figure 6 and 7. The sample did not chromatograph as well as the mixture of pure compounds did on the DB-5 column. In the case of the first two peaks, instead of symmetrical, gaussian shapes, rather broad, poorly shaped peaks were obtained. However, the same mass spectrum was obtained when different segments of the broad peak were scanned. Differences in the concentrations of the analyte solutions and/or interaction of the arsine sulfides with as yet unidentified minor components in the sample may be responsible for observed differences in the TIC's of AS90B and the mixture of pure compounds. The presence of steric isomers in the case DMEAS and MDEAS may also lead to the presence of incompletely separated peaks. Because of the asymmetry in the peaks, quantitation could not be achieved. In any case, comparison of Figures 4 through 7 shows that AS90B is essentially a mixture of TMAS, DMEAS and MDEAS with significant amounts of elemental sulfur, thus confirming results obtained by ^{1}H NMR measurements. The slight variations in retention times for a given compound are probably due to the manual injection technique used.

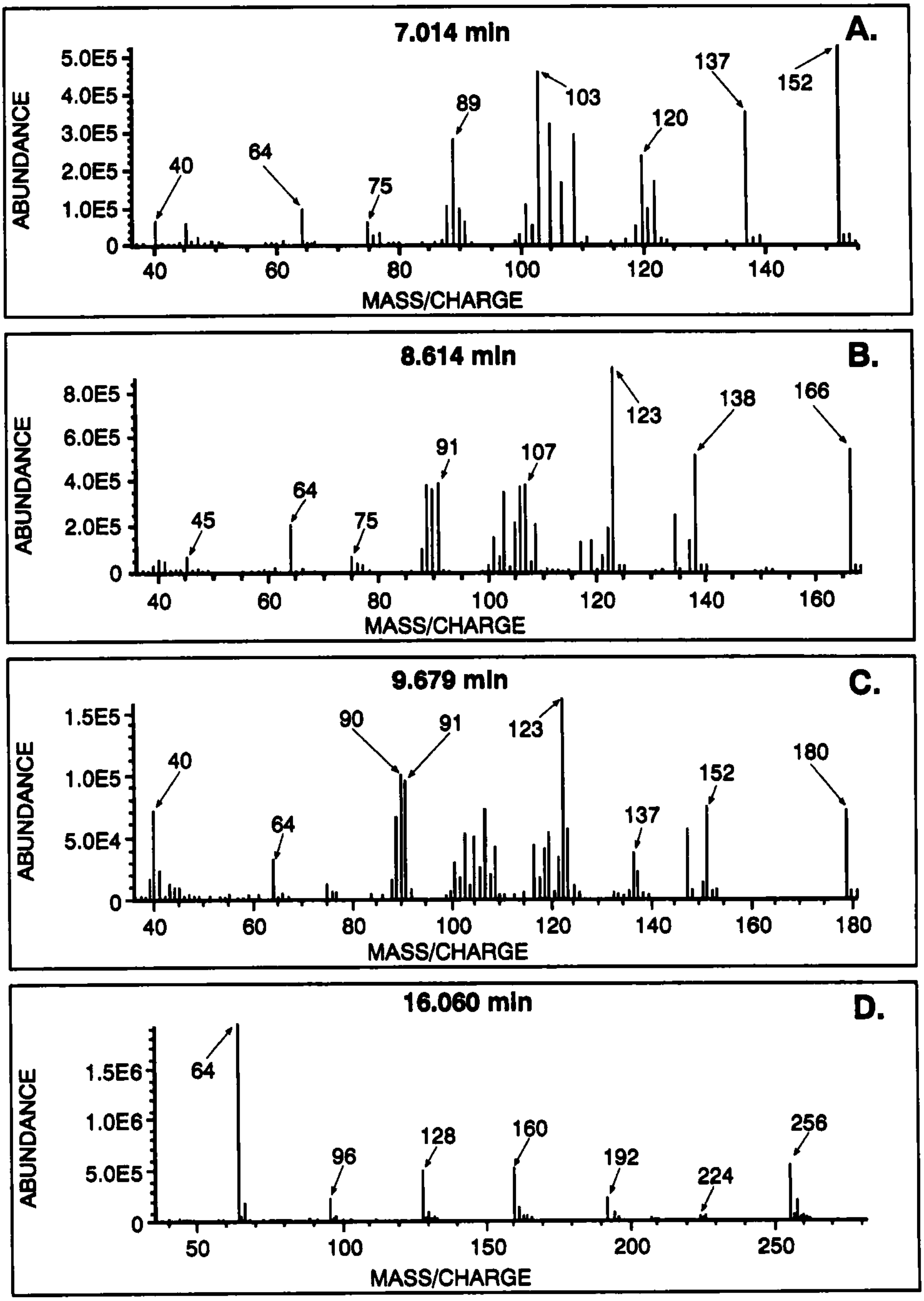

Figure 7 Mass spectra (with retention times) for pipeline solid (AS90B).

Reactions of trimethylarsine with sulfur compounds

Experiments were conducted for the purpose of gaining some insight into the mechanism by which the arsine sulfide deposits in the pipelines. TMA was chosen as the representative alkylarsine and its reactions with H_2S and other sulfur compounds under a variety of reaction modes were studied. The reaction conditions and the qualitative information gained is summarized in this section.

TMA dissolved in organic solvent and sparged with H_2S

One mL of TMA was dissolved in 50 mL of ethanol in a 125 mL gas dispersion bottle, with a medium porosity frit and a slow stream of H_2S was bubbled through the solution. The solvent was then removed under a stream of N_2. The solid residue was dissolved in chloroform and analyzed by GC-MS. The presence of molecular ion peak of 152 at a retention time of 6.95 min. confirmed the presence of TMAS. The experiment was repeated, replacing ethanol with tetrahydrofuran as the solvent and identical results were obtained.

The reaction of liquid TMA with liquid sulfur compounds

One mL of TMA was mixed with one mL of a sulfur compound (dimethyl sulfide, dimethyl disulfide, diethyl sulfide or diethyl disulfide) in a thick-walled glass cyliner which was then sealed. The cylinder was then kept in a water bath (50°C) for 24h. The formation of crystals was observed in every case. The mother liquors were stripped by a stream of N_2 and the crystals analyzed by GC-MS as before. In the case of dimethyl sulfide and dimethyl disulfide (Figure 8), there was clear evidence of the formation of TMAS. There was no evidence of TMAS formation in the other two cases. The retention times and the corresponding mass spectra of the other products appeared to be common to all the four cases and did not correspond to those of the other arsine sulfides. The spectra contained several higher mas ion peaks, e.g., 207, 221, 281 and 355. No attempt was made to identify these compounds.

Reaction of gaseous TMA with gaseous sulfur compounds

In these experiments gaseous TMA was mixed with H_2S or CH_3SH (both are gases under ordinary conditions) in the presence or absence of potentially catalytic materials. Any change in the pressure of the system was measured over a period of time. The reaction was carried out using the vacuum manifold (Figure 1). In cases where a change in pressure indicated the occurrence of a reaction, the contents of the reaction chamber were analyzed by suitable methods in order to identify the products.

In a typical experiment the vacuum manifold was evacuated and TMA was introduced through the charging valve into the two-liter reservoir and collected in the reservoir's cold finger cooled with liquid N_2. With the system again evacuated the TMA reservoir was opened and 150 torr of TMA was introduced into the reaction chamber and the excess TMA was collected in liquid N_2. By an identical procedure, 250 torr of H_2S was introduced into the reaction chamber. The reaction chamber was isolated from the rest of the mainfold and the course of the reaction was followed using the pressure transducer.

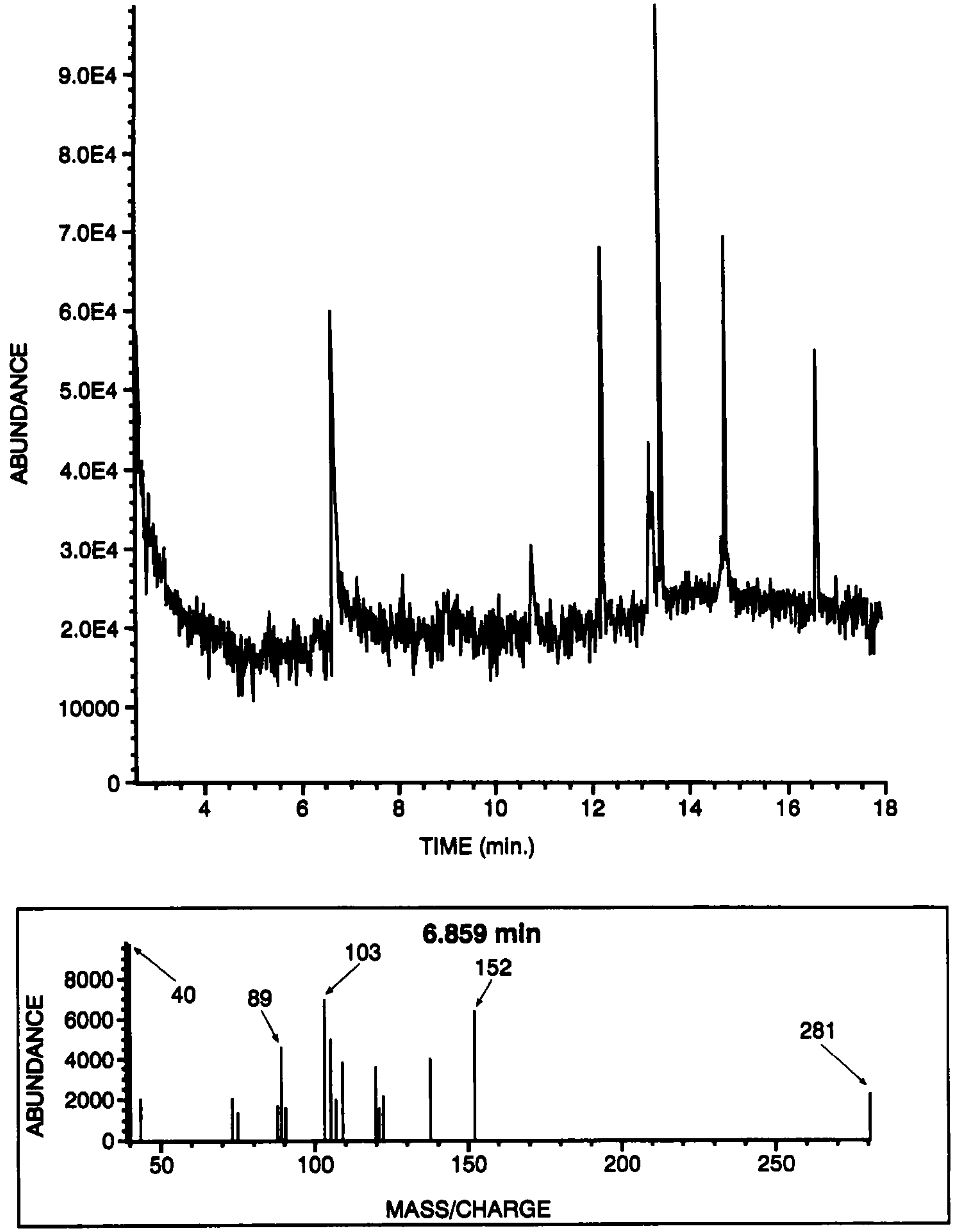

Figure 8 GC-MS spectrum of the reaction product of TMA with $(CH_3)_2S_2$.

Table 6 Reactions of gaseous TMA with gaseous sulfur compounds.

TMA pressure, torr	*Sulfur Compound, pressure, torr*	*Catalysts(s)*	*Pressure change in 12 h.*	*Remarks*
150	H_2S, 250	—	None	NA
125	H_2S, 200	2 mL of H_2O	None	NA
119	H_2S, 219	2 mL of H_2S + steel pipe filings, 5 g	344 to 289 torr	TMAS produced
100	H_2S, 200	Lateral pig residue, 5 g	None	NE
135	H_2S, 240	2 mL H_2O + Nickel, 5 g	None	NE
75	H_2S, 150	2 mL H_2O + Chromium, 5 g	241 to 206 torr	TMAS produced
150	CH_3SH, 250	—	None	NA

NA : No analysis performed.
NE : Analysis performed but no evidence of TMAS.

The experimental conditions and the results are summarized in Table 6. In all except one case, TMA and H_2S were the reactants. In only two cases was there clear evidence for the formation of TMAS as determined by GC-MS. The presence of steel pipe filings with H_2O or chromium metal with H_2O was successful in inducing the production of TMAS as determined by the GC-MS analysis of the chloroform extract. None of these "catalysts" by itself was successful in producing TMAS.

The results summarized in Table 6 suggest that, under field conditions the organo arsine sulfides are most likely formed by the reaction of H_2S with the respective organo arsine. The presence of both a metal substrate (iron or chromium) and H_2O appear to be necessary for this reaction to take place. Both these conditions are likely to be met in the pipelines.

Although the ^1H NMR method described was designed specifically for the analysis of the pipeline solids, it may be feasible to include this mehtod for the speciation of arsenic in the environment. It is well documented that alkylation reactions mediated by fungi and bacteria are an important mechanism for the mobilization of arsenic in the environment.[8] It is feasible that the organoarsines produced (most often $(CH_3)_3As$) can be trapped in an organic solvent containing elemental sulfur under suitable conditions to produce the alkylarsine sulfide. It is likely that long collection periods may be involved to bring the sample concentrations within the dynamic range of the ^1H NMR method.

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