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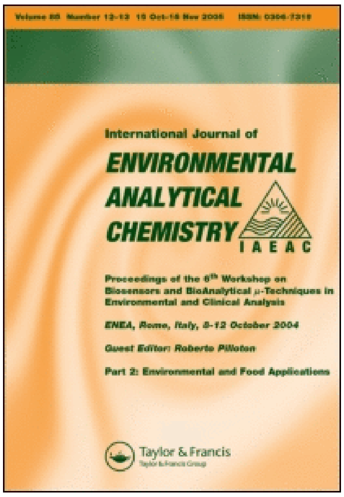

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ANALYSIS AND REMOVAL OF ARSENIC FROM NATURAL GAS USING POTASSIUM PEROXYDISULFATE AND POLYSULFIDE ABSORBENTS

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Natural gas from the large Abo gas field in southeastern New Mexico contains arsenic (0.2 to 2.5 µg/L) in the form of trialkylarsines. A method of analysis for arsenic which is based on the extraction of the alkylarsines into a saturated solution of potassium peroxydisulfate (PPDS) followed by determination of total arsenic, as AsO_4^{3-}, by hydride generation- d.c. helium plasma emission spectrometry (HG-DCHPES) is described. The extraction of the alkylarsines was carried out by either shaking 1L gas samples with PPDS or sparging the gas in PPDS solutions. Analytical results of acceptable precision can be obtained using either procedure. Temperature (24°–45°C) or pH (1.10–4.10) had little effect on the As concentrations obtained by the sparging method. The measured arsenic concentrations of natural gas samples stored in Cr-Mo steel cylinders decrease with time of storage (~30% in the first 4 weeks). A standard blend of trimethylarsine in CH_4 (1 mole TMA in 10^6 moles of CH_4), stored in nickel-containing steel cylinder, showed a similar decrease in As concentration with time. The measured arsenic concentrations increase when the temperature of a cylinder of natural gas is heated indicating that part of the alkylarsines may be present in a condensed or physically adsorbed form on the inner walls of the cylinder. Scanning electron microscopy with X-ray microanalysis of the metal powders (Ni, Cr, Mo, Fe) contacted with TMA indicate that arsenic-rich solids also containing C and O are formed in the case of Ni and Cr. This phenomenon may represent an additional factor in the observed decrease in As concentration with time of storage. Polysulfides in solution form (Na_2S_x) or solid (Na_2S_4) can quantitatively remove the trialkylarsines from natural gas.

KEY WORDS: Arsenic, natural gas, trialkylarsines, removal.

INTRODUCTION

Natural gas is the most important gaseous fuel resource in the world. In the United States natural gas supplies 20–25% of the nation's energy demand. The advantages of using natural gas as a fuel are gaining increasing recognition in an environmentally sensitive society. These advantages[1] can be summarized as follows:

- It is a clean burning fuel.
- It is relatively inexpensive.
- The natural gas resources of the world are abundant.

With these advantages in mind, we can foresee an increasing use of natural gas, primarily as a fuel, in a variety of sectors. It is also likely that the "unconventional"[2,3] sources of natural gas such as the "tight sands" and the Devonian shale will be exploited to a greater degree in the near future. With the exploitation of natural gas from differing geological origins, gas quality, and in particular, the presence of trace contaminants[4] becomes a legitimate concern. The presence of some (hazardous) contaminants like H_2S and other sulfur compounds has been recognized for a long time and corrective technology for their removal has been employed in the gas industry[5]. As environmental concerns increase and as sensitive analytical instrumentation continues to develop, the presence of several low level contaminants including radon, Pb and arsenic has been discovered[6]. The presence of some contaminants, e.g. arsenic, is considered to present a potential health hazard, but it may also interfere with the normal operation of distribution systems. Concurrently, there is a strong need for the development of reliable analytical methods for the determination of the low levels of these elements in the natural gas matrix.

Origin of arsenic compounds in natural gas

Among the trace elements ordinarily associated with fossil fuel deposits, arsenic occupies a somewhat unique position in that probable biogeochemical mechanisms of its occurence have been suggested. In seawater, the concentration of arsenic is very low, ≈ 2μg per liter. However, marine organisms are known to have the ability to concentrate arsenic several thousand times the levels in ambient seawater, [7] the average being 2g arsenic per kilogram dry weight of the organism. These organisms convert the inorganic arsenate present in seawater to complex organoarsenic compounds such as arsenobetaine, arsenocholine, arsenolipids and arsenosugars.[7,8] It is logical to assume that the paleoorganisms that lived in marine or lacustrine depositional environments would have had the same ability. Following their death and subsequent accumulation with other sediments these arsenic-containing materials, could, under favorable conditions, develop into source beds from which petroleum products would be formed. The formation of petroleum is accompanied by the production of methane which is the principal component of natural gas. It is probable that at the pressure, temperature and the reducing conditions prevailing in the gas formation, the complex organic compounds are likely to have undergone a series of alkylation-dealkylation and decarboxylation reactions producing volatile trialkylarsines which would partition with the natural gas.[7]

Microbes, which are known to survive extremes of heat or cold, can serve as an alternative source of the organoarsenic compounds in natural gas. It is well known that a number of microorganisms are capable of methylating inorganic arsenic to alkylarsines.[9]

Formation of trialkylarsine sulfides in the gas pipelines

We first became aware of the presence of arsenic compounds in natural gas in 1987 when a major gas producer consulted with us on possible methods for their removal. The problems relating to the presence of arsenic first surfaced in the gas distribution pipeline system of a western gas utility company when powdery white solids were being deposited in the vicinity of the gas pressure regulating equipment. These solids contained 40–50% arsenic principally of R_3As, $R = CH_3, C_2H_5$. These deposits caused the equipment to malfunction either causing

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an outage or dangerous overpressurisation. The contaminated gas was eventually traced to the Abo gas field in southeastern New Mexico. In 1989, we undertook an investigation to develop methods for the analysis and removal of arsenic in natural gas.

In an earlier publication,[7] we described the identification of trialkylarsines (principally trimethylarsine) to be the source of arsenic in natural gas. An analytical procedure for the determination of the total arsenic which involved the extraction of the trialkylarsines contained in 1 dm^3 of the natural gas into 10 cm^3 HNO_3 was described. The flask containing the gas and the acid was shaken on an orbital shaker for 1 hour. The resulting solution was heated with concentrated H_2SO_4 to complete the conversion of the arsenic compounds to arsenate. The total arsenic in the mineralized solution was determined by hydride generation followed by d.c.-helium plasma emission spectrometry (HG-DCHPES). In this paper we describe an analytical method for the determination of total arsenic based on the extraction of the organoarsines from natural gas with a saturated potassium peroxydisulfate, $K_2S_2O_8$, solution. In addition to being a powerful oxidizing agent, peroxydisulfate offers several advantages over HNO_3: first, the use of caustic reagents like concentrated HNO_3 and H_2SO_4 is avoided. This is a considerable advantage in view of the fact that sample collection and preparation will have to be done at the wellhead location where the facilities may be primitive and by personnel who may not be trained chemists. Second, as H_2SO_4 boils at 338° C there is a long cooling time before the samples can be handled. Dilution also produces heat which must be allowed to dissipate before sample solution can be made up to volume. Lastly, the presence of oxides of nitrogen which are produced by the disproportionation of nitric acid is avoided. Nitrogen oxides have been shown to cause major interferences in arsine generation methods.[10]

The analytical method was developed for operation in two modes, the discrete sample mode and the sparging mode. In the discrete sample mode, a vacuum manifold was used to collect four replicate samples of the gas simultaneously. In the sparging mode, natural gas was passed through a series of gas dispersion bottles containing the absorbent solution via a calibrated flowmeter for known intervals of time. The effects of several variables including temperature and pH were examined. In addition to $S_2O_8^{2-}$, the suitability of sodium polysulfides (Na_2S_x and Na_2S_4) as absorbents for organoarsines was investigated. The total arsenic (as arsenate) concentrations in the absorber solutions or the outlet gas were measured by HG-DCHPES. The implications of the non-availability of an analytical standard for organoarsines in a hydrocarbon matrix are also discussed.

MATERIALS AND METHODS

Reagents

Potassium peroxydisulfate ($K_2S_2O_8$) was Baker Analyzed Reagent grade or EM Reagent grade with heavy metal impurities reported as less than 0.0002% in either case. Although the pH of the saturated $K_2S_2O_8$ solutions varied between 2.5 and 3.5 depending on the source, no other differences in behavior were observed. For hydride generation, 4% $NaBH_4$ (Aldrich 99%) solutions in 1% NaOH were used.

All other reagents used were either reagent grade or recrystallized from commercial grade reagents.

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Ultrapure water with a resistance of 17.6 megohms/cm from a Sybron/Barnstead Nanopure II still was used for the preparation of all solutions.

The sources of the natural gas were wellheads in the Abo gas field of southeastern New Mexico. The samples from the two sources used were labelled WPG and WG. They were received in 22L chromium-molybdenum steel cylinders pressurized to 750 psig at the wellhead.

A Corning Model 250 Ionanalyzer pH meter was used for pH measurements.

Collection and preparation of discrete samples

As in our earlier publication,[7] a 1L round-bottomed flask fitted at the center with a 24/40 ground-glass neck and a sidearm with a Teflon or Pyrex stopcock was used for collection of gas samples from the cylinders. However, for the purpose of obtaining greater precision some important changes were introduced into the procedure. In the earlier procedure, the evacuated 1 liter flasks had been individually filled with natural gas until the pressure inside the flask was slightly above the atmospheric pressure as judged by the analyst's hand on the stopper of the flask. The HNO_3 solution was then added after removing the stopper and quickly inserting the bottom (with a matching ground joint) of a 50.0 mL graduated dropping funnel containing the solution. We felt that these steps might possibly introduce a subjective

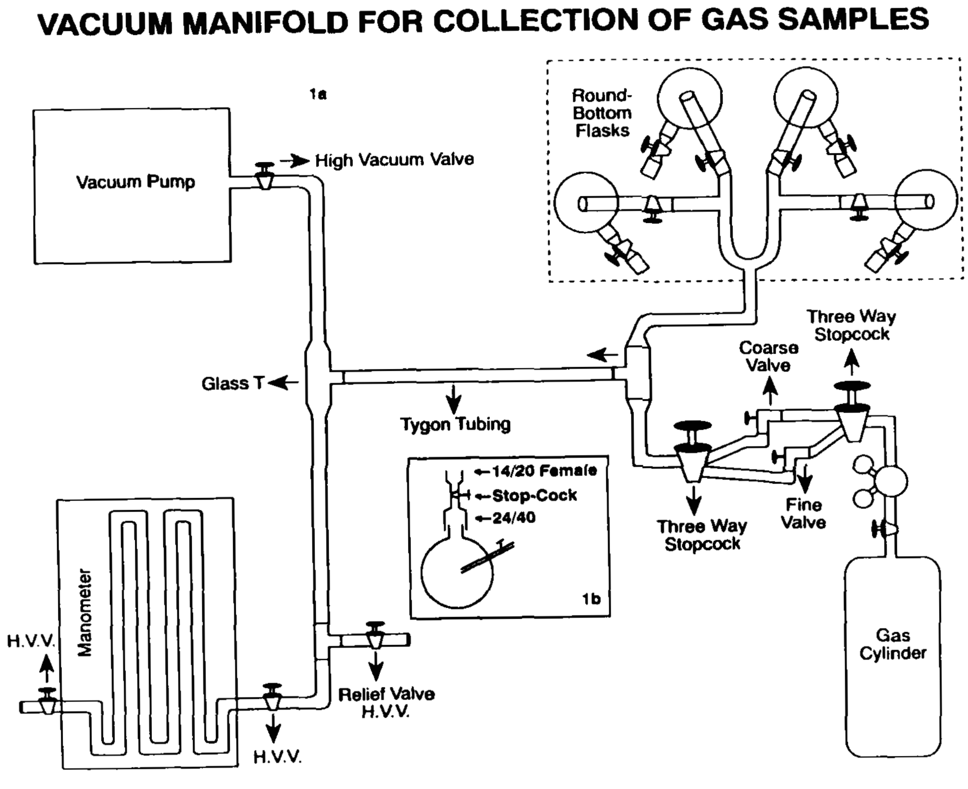

Figure 1a Vacuum manifold for the simultaneous collection of four 1L gas samples.
Figure 1b Collection flask with adapter.

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error with respect to the pressure inside the flask and there is introduced the risk of dilution by air. The flasks were, therefore, redesigned to prevent the ingress of air during addition of the peroxydisulfate solution (Figure 1b). A vacuum manifold (Figure 1a) with a 1 meter N-type mercury manometer designed to fill four flasks simultaneously was constructed. The adapters were secured to the flasks with springs and the four flasks were connected to the manifold and evacuated. The flasks were then flushed with natural gas from the cylinder, reevacuated and refilled with natural gas to a pressure of 760 mm of Hg as indicated by the manometer. After closing the stopcock in the sidearm, each flask was disconnected from the manifold and fitted to the bottom of the dropping funnel containing the saturated potassium peroxydisulfate solution (PPDS). The stopcock in the adapter was opened and 20 mL of the solution was carefully introduced in increments by opening the stopcock in the graduated dropping funnel, swirling the contents after each addition. After the addition was complete, the stopcocks were closed and each flask with the adapter was disconnected from the dropping funnel. The flasks were clamped on a Lab-Line Junior Orbit platform shaker and shaken at 350 rpm for one hour. The contents of each flask were then quantitatively transferred to a 250 mL beaker using several additional rinses for a total of 15 mL of PPDS as rinse. The solutions were gently boiled in the covered beakers for an hour and water was added as necessary. After cooling, each solution was made up to volume (50.0 mL) and analyzed for arsenic.

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Sparging

The pH of the PPDS solution was adjusted by adding concentrated H_2SO_4 or NaOH solution. Four 125 mL bubblers, each with gas dispersion tube of medium porosity and containing 100 mL of the absorbant solution, were connected in series and immersed to an appropriate level in a thermostated bath containing 50% ethylene glycol. The temperature of the bath was maintained with the aid of a Brinkman, MGW Lauda RC2 circulating bath. The sample gas source was connected to the absorber train via a Cole Parmer Model NO42, 150 mm variable area flowmeter. The flowmeter was calibrated by measuring with a stopwatch, the rate of displacement of a 25.0 mL or 10.0 mL column of air in a 50.0 mL or 10.0 mL buret segmented by a soap film. For each setting of the flow meter, the flow rate was measured three times and then averaged. The per cent RSD for the replicate measurements varied from 0.09 at 10.2 mL/min to 0.71 to 81.6 mL/min. A linear relationship was observed between the logarithm of the flowmeter reading and the logarithm of the flow rate.

In a typical experiment, temperature equilibration was obtained by passing purified helium or nitrogen through the absorber train for one hour. The the sample gas was bubbled through the bottles at the required flow rate to give a total gas volume of 1.00 L. The content of each bottle was then collected and boiled for one hour and individually analyzed for arsenic by HG-DCHPES as before. In the case of the experiments where Na_2S_x was the absorber, it was not feasible to analyze the solutions themselves because of interference in the HG-DCHPES procedure. Instead, 1.00 L of the sample gas was bubbled through 100 mL of Na_2S_x solution in a 125 mL gas wash bottle and the outlet gas was collected in an evacuated 1 L flask and analyzed as before for arsenic. The manifold was used for evacuating the flask and refilling with the exiting gas. There was excellent agreement between the time required to attain a pressure of 760 mm Hg in the system as indicated by the manometer and that calculated by the flow rate. The experiment was repeated adding Na_2S_x absorber bottles sequentially and the minimum number of bottles necessary for removal of 95% of the arsenic was determined.

Determination of arsenic by hydride generation

The analyte solutions were analyzed by HG-DCHPES by monitoring the intensity of the arsenic emission line at 228.8 nm. The details of the instrumentation and procedure have been described elsewhere[11]. The instrument was calibrated before each use with standards prepared by diluting a 1000 ppm. arsenic standard (J. T. Baker Intra-analyzed, 99.999% spectrally pure As (III) oxide in 0.3 M HCl).

Modifications of the original procedure were made to reduce the analysis time from 15 minutes to 4 minutes. For each set of analyses, a correction for the presence of background arsenic was applied by carrying a blank solution through all the steps. This is a very sensitive technique and under optimum conditions detection limits of 1 ng or less can be achieved.

RESULTS AND DISCUSSION

Analysis of pure organo-arsenic compounds

The method for the analysis of total arsenic in natural gas can only truly be validated with certified standard samples containing known amounts of arsenic in a hydrocarbon matrix. At the present time, our efforts to prepare, purchase or obtain such stable standards have not been successful most probably due to the reaction of the organoarsines with the walls of the container. This topic is discussed in later section. Since it has not yet been possible to validate the method overall (with a reliable standard) it is important to examine the reliability of the steps comprising the analysis. The reliability of the final step, i.e., the determination of inorganic arsenic by HG-DCHPES is well established. The first step is the extraction of the arsines from the gaseous phase to the PPDS solutions under the conditions of the analysis. In the absence of a certified standard sample the efficiency of this step is difficult to demonstrate. The second step involves the conversion of the organic arsines to the inorganic arsenate by PPDS which involves the rupture of C-As bonds. To demonstrate the completeness of this step, known solutions of methane arsonic acid (MAA), dimethylarsinic acid (DMAA) and trimethylarsine sulfide (TMAS) were mineralized with PPDS and the resulting solutions analyzed by HG-DCHPES. The results are shown in Table 1.

The results given in Table 1 clearly show that, under the analytical conditions, the organo-arsenic compounds tested are quantitatively converted to AsO_4^{3-} by PPDS. This is in good agreement with observations in the literature regarding the effectiveness of $S_2O_8^{2-}$ in decomposing organoarsinic compounds. In developing an atomic absorption method for determining total arsenic in aquatic samples, Fishman and Spencer[12] reported the quantitative recovery of arsenic from phenylarsonic acid, disodium methane arsonate (DSMA) and dimethylarsinic acid in an automated persulfate digestion procedure. Newberry[13] also

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Table 1 Arsenic recoveries after mineralization with PPDS.

Compound	*Mass, g*	*Dilution factor*	*As in analyte*	
			Theoretical, ng	*Experimental, ng*
MAA	0.2443	3.33×10^6	39.2	41.1 (±0.1) (104.7%)[a]
DMAA	0.0845	1.67×10^6	36.7	38.8 (±0.1) (105.7%)
TMAS	0.01653	2.08×10^5	39.2	38.6 (98.5%)
TMAS	0.01788	2.23×10^5	39.5	39.3 (99.5%)

[a] Percent recoveries.

found persulfate digestion to be effective in recovering arsenic quantitatively from a number of organo-arsenic compounds for titrimetric analysis.

Analysis by discrete sampling method

Natural gas samples, TWP and WG were analyzed by the discrete sampling procedure and the results for the TWP gas are given in Table 2. On each of the dates 1 L samples were analyzed in quadruplicate. Despite the somewhat high standard deviations, it is evident that the measured average As concentrations decrease with the length of the time the gas is stored in the cylinder.

In order to examine this phenomenon further and to explore the feasibility of making available a certifiable standard for volatile arsenic in a hydrocarbon matrix, we requested Matheson Gas Products, Gloucester, MA., to prepare a blend containing a known amount of trimethylarsine in methane. The blend was received in a Matheson ultraline cylinder (1000 psig) whose inner surface had been polished and plated with non-porous Ni having a thickness of a few microns. Identical cylinders have been found to be effective in preserving blends of AsH_3 by Matheson Gas Products. The blend was certified to contain 1.5 moles (±20%) of TMA in 10^6 moles of CH_4 which translates to 4.7±0.94μg/L. The "standard" blend was first analyzed (Feb. 21, 1991) and again two days later (Table 3). The results are in very good agreement with the expected value and well within the range of variability claimed by the manufacturer. However the analysis carried out 5 weeks later shows a steep decline in the measured concentration (HG-DCHPES instrument response remained normal) and after 22 weeks, the residual arsenic was only about 5% of the original value. The decrease in the

Table 2 Variation of arsenic concentration in TWP natural gas with time of storage.

Date of analysis	*Range of As Conc. ng/L*	*As conc. average ng/L*	*Rel. std. dev %*
Sept. 18, 1991	2402–2664	2500	4.6
Sept. 16, 1991	1671–2505	2162	16.5
Oct. 3, 1991	1896–2347	2147	9.7
Oct. 6, 1991	1382–1963	1689	17.3

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Table 3 Variation of total arsenic concentration of CH_4-$(CH_3)_3As$ blend with time of storage[a]

Date Analyzed	*As Conc., ng/L*
Feb 21, 1991	4080±50
Feb 23, 1991	4480±50
March 23, 1991	1500
June 8, 1991	197±32
July 15, 1992[b]	147±4

a. Certified value: 4700±940 ng/L

b. Analyzed by sparging method.

arsenic concentration of the "standard" blend is similar to the precipitous (1 or 2 orders of magnitude in a week) decline in the arsenic content of natural gas samples shipped in 304 stainless steel bottles that had been observed previously[7].

We have not yet been able to definitely identify the factor(s) responsible for the loss of arsenic from gases stored in Cr-Mo steel cylinders and cylinders made with Ni-containing steels. This phenomenon is clearly of importance as it relates to the study of arsenic in natural gas and we are continuing this effort. Some of the possible explanations for the variability of the measured arsenic concentrations are the following:

i. Because TMA (b.p. 54°C) and the higher alkylarsines have boiling points higher than room temperature, they may undergo condensation if suitable nucleating conditions are available.

ii. The mixture of alkylarsines and the hydrocarbons is not homogenous. As an example, part of the arsenic may be present in a particulate form.

iii. The alkylarsines may be physically adsorbed on the walls of the cylinder. This is more likely to occur in the case of cylinders where the walls have not been polished or have not been plated with a non-porous metal.

iv. The arsines may be chemisorbed on the cylinder walls. A possible mechanism for this could be the formation of solid compounds such as $Cr(Me_3As)_6$ and $Ni(Me_3As)_4$. The formation of these compounds is possible as they are analogous to metal carbonyls.

v. The formation of highly reactive FeS by the reaction between iron and the sulfur compounds is well known in the gas industry. Arsines are known to react with sulfur to form arsine sulfides $R_3As{=}S$. Hence it is likely that FeS can function as an active source of sulfur for this reaction to take place.

It is possible that several of the foregoing factors may be responsible for the observed changes in the arsenic concentrations. It is reasonable to conclude that if the variability is due to the presence of particulate arsenic, the concentrations would fluctuate rather than decrease steadily. The absence of particulate As was confirmed by analyzing the TWP gas by the discrete sampling method after it was filtered through a Whatman 0.45 u glass microfiber filter. No significant differences were noted in the concentrations of the filtered and unfiltered gases (agreement within 2%) and it can be concluded that arsenic is not present in a particulate form.

If the arsines are partly or wholly present in a physically adsorbed or condensed form, it is reasonable to expect that the measured arsenic concentrations will show a dependence on

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Table 4 Effect of the temperature of WG natural gas on measured arsenic concentrations.

Temperature °C	*Range of As Conc., ng/L*	*As Conc. average, ng/L*
0	94–161	130
24	192-273	233
50	313-317	315
50	252–340	297

the temperature of the cylinder and its contents. In order to test this hypothesis a cylinder (Cr-Mo) of WG gas was equilibrated at 3 temperatures 0, 24, and 50 °C and the gas analyzed by the discrete-sampling method. An approximate temperature of 0°C was obtained by leaving the cylinder outdoors overnight when the ambient temperature was 0°(±2)C. A large waterbath (4′x3.5′x2.5′) in which thermostated water was circulated through a copper coil was used to obtain the other temperatures. An immersion time of 6h was used for temperature equilibration. The results given in Table 4 show a large degree of scatter, but there is noted a definite trend of lowered arsenic concentrations with decreasing temperatures.

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Sparging experiments

The purpose of these experiments was to develop a more rapid method for the extraction of analyte gas samples for analysis by HG-DCHPES. The sparging method is much simpler to carry out than the discrete sample method and involves only the sparging of a known volume of gas through the absorber towers. The peroxydisulfate solutions in the absorber towers are analyzed and the sum of the arsenic contents of each of the four towers gives the arsenic content of the volume of gas taken.

Among the parameters most likely to influence the rates of oxidative reactions of $S_2O_8^{2-}$, the pH and the temperature of the absorber solutions were studied. It was important to conduct the comparative experiments in as short a time frame as feasible in view of the decreasing arsenic content of the natural gas with time of storage in the cylinder. The results of the experiment on the effect of pH on the analysis of TWP gas are given in Table 5. The

Table 5 Effects of pH on arsenic analysis by sparging method.[a,b,c]

Bubbler	*pH=1.10 As, ng/L*	*pH=2.10 As, ng/L*	*pH=3.16 As, ng/L*	*pH=4.10 As, ng/L*
No. 1	872	1,006	833	966
No. 2	329	496	622	389
No. 3	470	121	252	322
No. 4	362	309	289	389
Totals, ng/L	2033	1,932	1,996	2,066

a. Flow rate=37.4 mL/min.

b. T=24°C,

c. As Conc. by 'Discrete Sampling' method: 2000 ng±100 ng/L

Table 6 Effects of temperature arsenic analysis by sparging method.[a]

Bubbler	*14°C* *As, ng/L*	*24°C* *As, ng/L*	*35°C* *As, ng/L*	*45°C* *As, ng/L*
No. 1	598	835	1,196	368
No. 2	102	529	412	195
No. 3	247	329	412	1,277
No. 4	143	216	0.0	119
Totals, ng/L	1,090	1909	2,010	1,959

a. Experimental conditions: Flow rate, 16.7 mL/min; t=60 min; pH, 2.10

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preparation of all the samples and the analysis were completed during an eight-hour period. For purposes of comparison the results of a discrete sample analysis carried out during the same period are also given. The variation of pH does not appear to influence the analytical results in a significant way with the possible exception that arsenic content of the first bubbler is the highest at pH 2.10. The mean arsenic concentration (averaged over the analyses at the 4 pH values) is 1984±47 ng/L which is in excellent agreement with the value obtained by the discrete sampling method (2000±100 ng/L). It is somewhat surprising that the arsenic content of bubbler No. 4 is higher than that bubbler No. 3 in three out of four cases. A reasonable explanation is that the gas dispersion tubes are not uniform in porosity. This leads to differences in gas-solution contact times in the bubblers. When the positions of the last two bubblers were interchanged, the trend was reversed.

The results of the sparging experiments at different temperatures are given in Table 6. Except at 14°C, when the measured arsenic concentration showed a 45% decrease, variation of temperature within the experimental range appears to have little effect. It is likely that raising the temperature of the absorber solution may decrease the solubility of TMA which compensates for the increased rate(s) of reaction(s) at the higher temperatures.

Removal of trimethylarsine from natural gas with sodium polysulfide

The results of the experiments to test the usefulness of Na_2S_x (solution) and Na_2S_4 (solid) as reagents to remove TMA are given in Table 7. The results indicate that polysulfide in either form is efficient in scrubbing TMA from natural gas. As expected, the gas flow rate has a strong influence on the efficiency of scrubbing, with just one bubbler able to remove 97% at the lower flow rate while three bubblers are required to achieve a comparable efficiency at the higher flow rate. Na_2S_x in the solid form is surprisingly efficient in removing TMA, with ~6.0g in two tubes sufficient to remove 98% of TMA. The addition of a third tube increases the efficiency only marginally.

Examination of metal powders exposed to TMA by scanning electron microscopy

In order to get some insight as to any possible chemical interactions between TMA and the cylinder wall materials some qualitative experiments on the effect of exposing pure metal

Table 7 Extraction of arsenic from TWP natural gas using polysulfides.[a]

	Na_2S_x (solution) as absorber			
Number of bubblers	1^b	2^b	3^b	1^c
[As] in outlet gas, ng/L	173	173	68	41
% As extracted	85.3	85.3	94.2	97

Numbers of tubes and g of Na_2S_4 used	*Na_2S_x (solid) as absorber$_b$ [As] found, ng/L in outlet gas*	*% As extracted*
(1 tube)~3.0g	339	71
(2 tubes)~6.0g	23	98
(3 tubes)~9.0g	16	99

a T=25°C
b Flow rate=16 mL/min
c Flow rate=8 mL/min

powders to TMA were done. Approximately 5 g of the metal powder (Ni, Cr or Mo) was taken in a heavy glass cylinder (3″×1″) equipped with a Teflon vacuum stopcock. The cylinder was connected to an all-glass vacuum manifold and the system evacuated. Trimethylarsine, in gaseous form, was introduced into the cylinder containing the metal powder (Ni, 75 torr; Cr, 135 torr; Mo, 235 torr) and the stopcock closed. The cylinder was removed from the manifold and kept (with the stopcock closed) in a vacuum oven for 24 h and outside the oven another 48h. There was formed a thin layer of a white crystalline material on the surface of the powders as well as on the walls of a cylinder. The metal powders were then transferred to other receptacles. Each of the original containers was washed with chloroform and the solvent was stripped from the extracts. The samples obtained were examined with the help of a JEOL JSM6400 scanning electron microscope equipped with a Tracor-Northern Model I-2 energy dispersive X-ray spectrometer. The discussion of the results is limited to nickel and chromium because of the apparent lack of interaction between molybdenum or iron and TMA. The energy-dispersive X-ray spectra of nickel and chromium powders before exposure to TMA indicated a high degree of purity and the absence of any arsenic impurity. The EDS of the nickel powder is shown in Figure 2. In Figure 3 are shown the cauliflower-shaped nickel particles exposed to TMA and the presence of an arsenic rich, white, crystal. The corresponding EDS are given in Figures 4 and 5. There is evidence for the presence of arsenic as a solid surface phase on the nickel particle. The presence of carbon and oxygen in the arsenic rich particle suggests that it could be $(CH_3)_3AsO$. The electron micrographs in Figures 6 and 7 depict two morphological forms of the crystals obtained from the $CHCl_3$ extract of the Ni-$(CH_3)_3As(g)$ system. The corresponding EDS spectra are given in Figures 8 and 9. Both the lath-shaped crystals (Figure 6) and the books of rhomboidal crystals (Figure 7) show strong As, C and O signals while the rhomboidal crystals also indicate the presence of significant amounts nickel. As the extract was not filtered through a microporous filter before the solvent was stripped, it is not certain at this time whether this represents the presence of a true metallo-organic compound containing nickel and arsenic or that the nickel signal is caused by the presence of particulate nickel. This aspect is being investigated further. In Figure 10 is shown the electron

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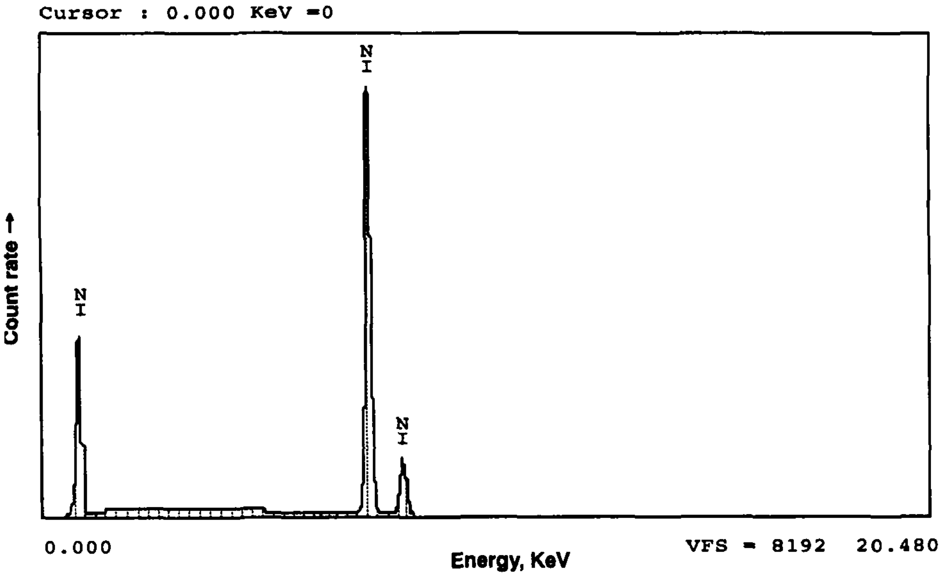

Figure 2 Energy-dispersive X-ray spectrum of nickel powder before exposure to trimethylarsine.

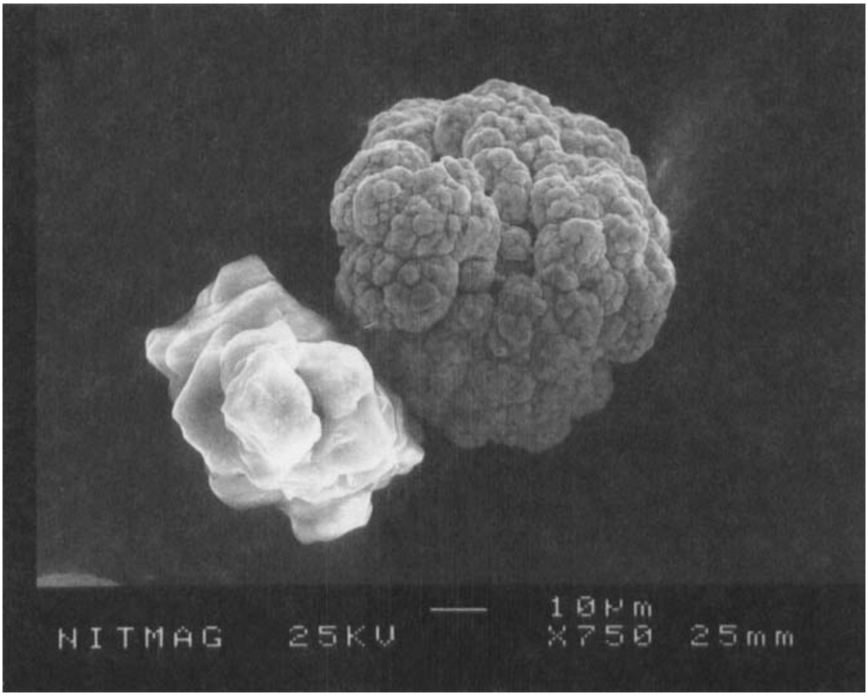

Figure 3 Electron micrograph of nickel particle (right) and arsenic rich particle.

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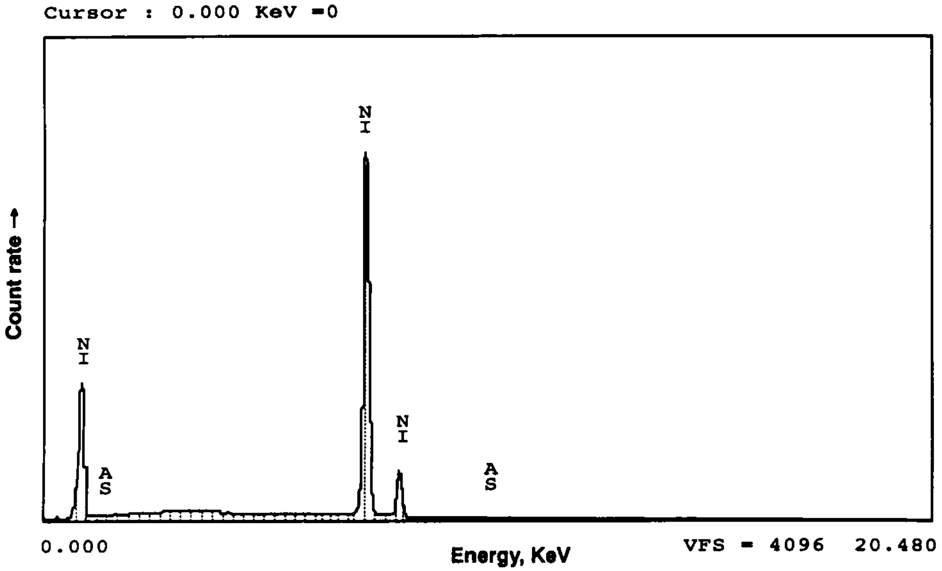

Figure 4 Energy-dispersive X-ray spectrum of nickel particle in Fig 3.

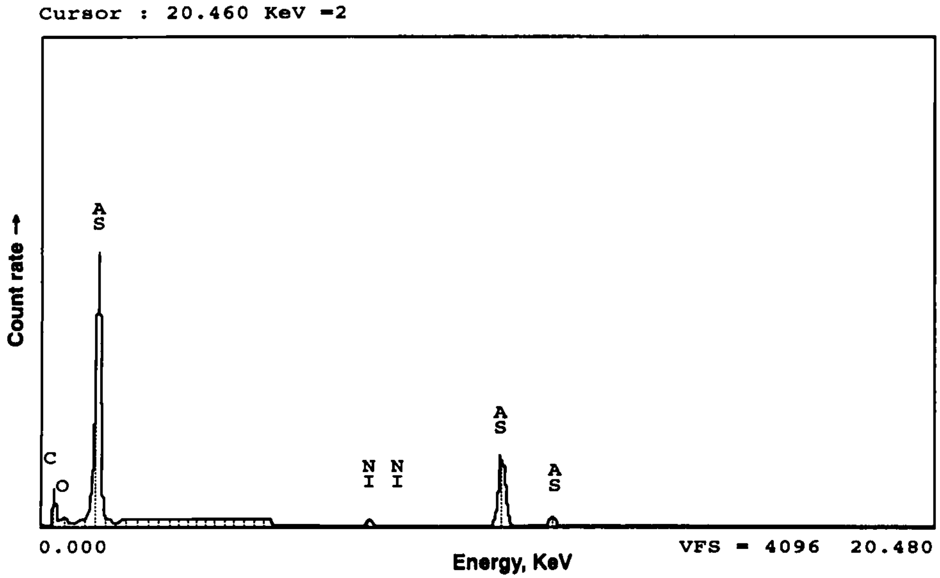

Figure 5 Energy-dispersive X-ray spectrum of arsenic-rich particle in Fig 3.

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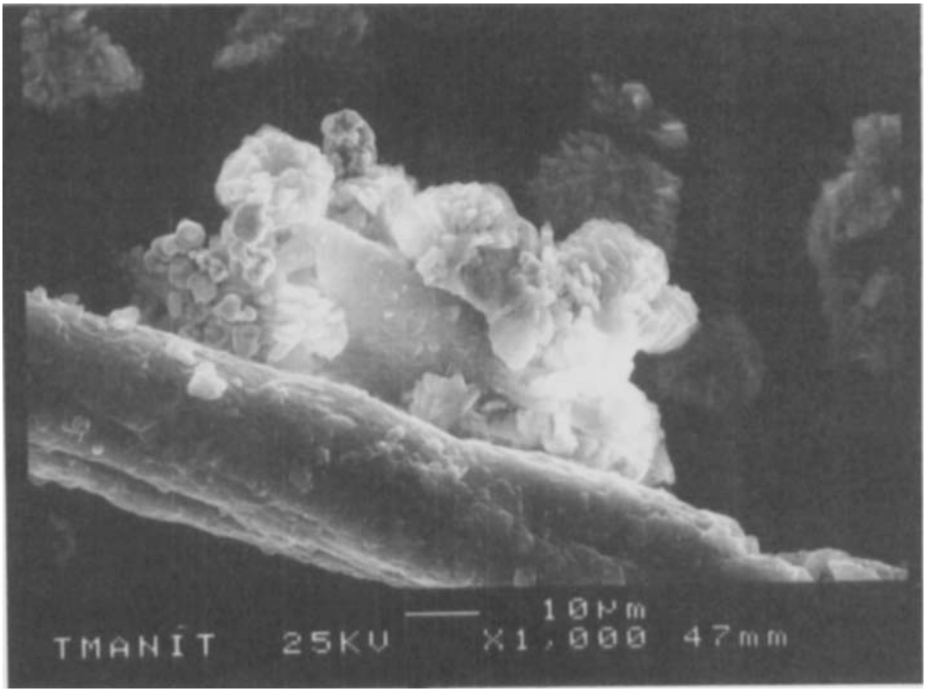

Figure 6 Electron micrograph of lath-shaped, arsenic-rich particle obtained from CHCl3 extract of nickel powder exposed to TMA.

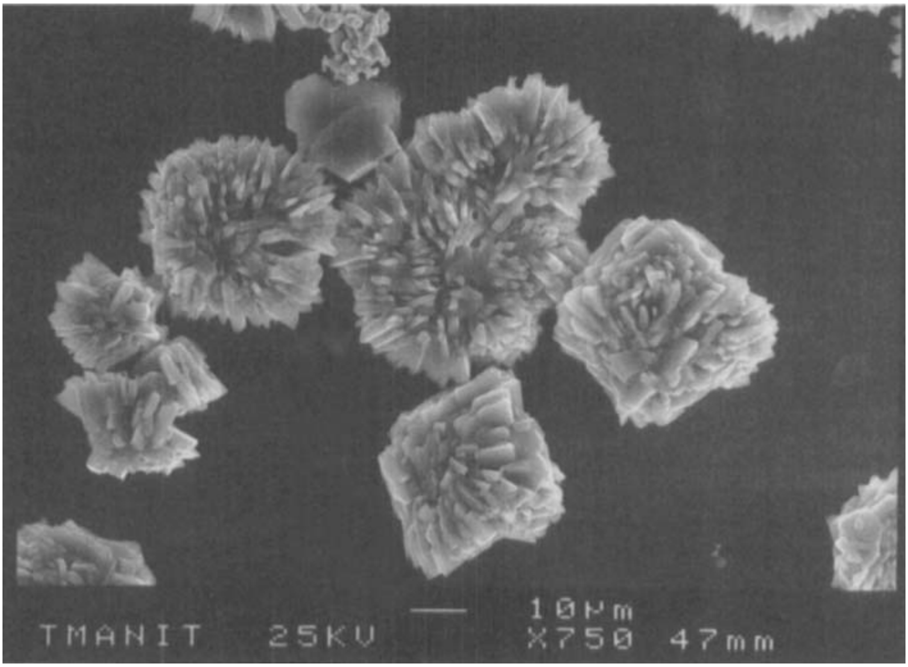

Figure 7 Electron micrograph of books of rhomboidal crystals obtained from CHCl3 extract of nickel powder exposed to TMA.

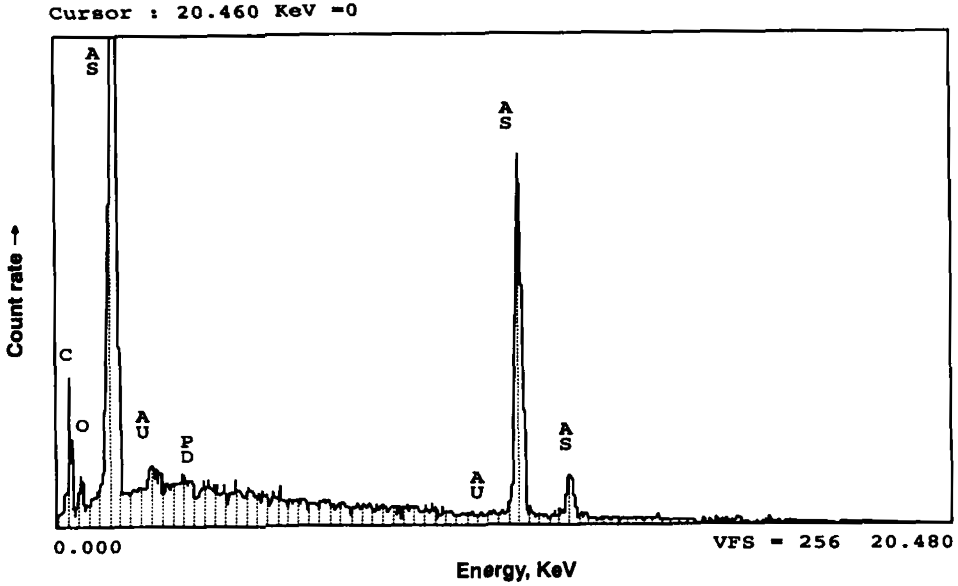

Figure 8 Energy-dispersive X-ray spectrum of particle in Fig. 6.

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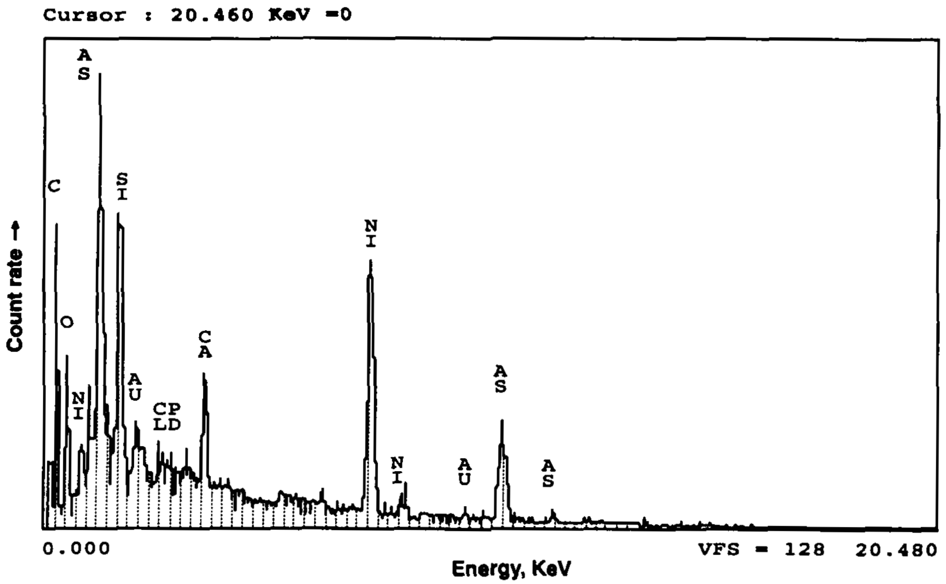

Figure 9 Energy-dispersive X-ray spectrum of rhomboidal crystals in Figure 7.

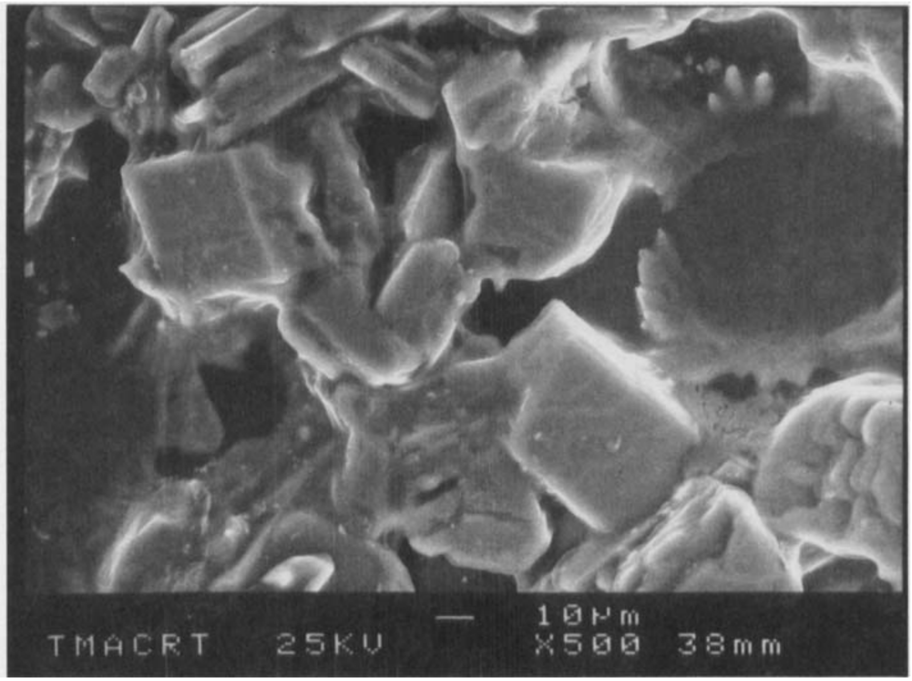

Figure 10 Electron micrograph of rhomboidal crystals obtained from CHCl3 extract of chromium powder exposed to TMA.

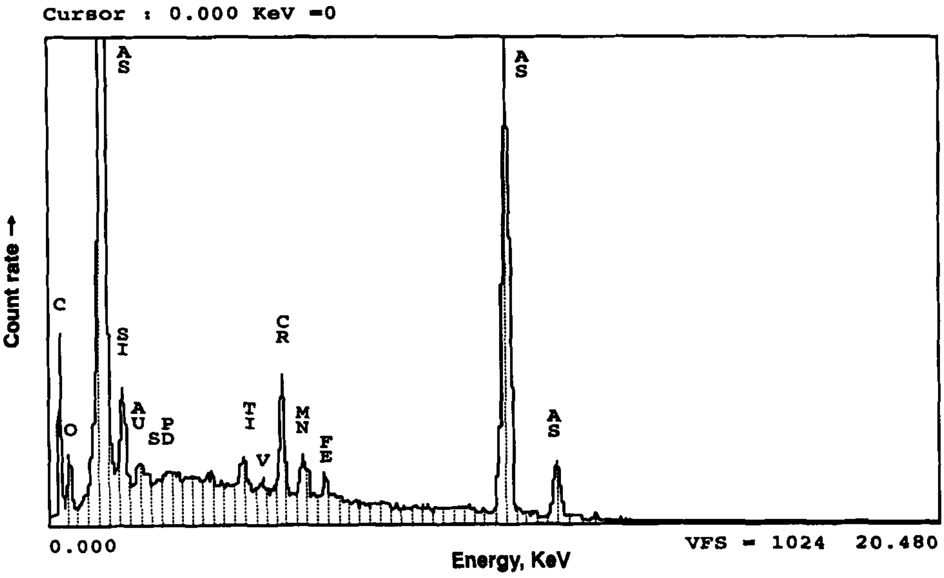

Figure 11 Energy-dispersive X-ray spectrum of crystals in Figure 10.

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micrograph of the rhomboidal crystals obtained from the $CHCl_3$ extract of Cr-$(CH_3)_3As(g)$ system. These crystals are much larger than the individual crystals in the books seen in the case of nickel. The corresponding EDS spectrum in Figure 11 again indicates the arsenic signals with C and O peaks present. There is a small Cr peak present.

CONCLUSIONS

Total arsenic concentrations in natural gas samples can be determined with acceptable precision by extraction into saturated potassium peroxydisulfate solutions and analysis by HG-DCHPES. Despite the non-availability of stable standards for arsenic in a hydrocarbon matrix for validation, it is very likely that the method is also accurate for the following reasons:

Peroxydisulfate quantitatively converts a number of organoarsenic compounds to AsO_4^{3-}. There is excellent agreement between the expected arsenic concentration of the CH_4-$(CH_3)_3As$ blend and the experimental value if the blend is analyzed within a few days of its preparation.

There is good agreement between the arsenic values obtained using the two methods of extracting the organoarsines from the natural gas, i.e., discrete sampling (shaking) and sparging.

The mechanism of the apparent decrease in the measured arsenic concentrations with the passage of time on storage is not clear. The increase in the measured arsenic concentration with increasing temperature of the cylinder suggests that physical adsorption or condensation may be involved. On the other hand, there appears to be some specificity associated with the metal powders with respect to their ability to act as substrates for the formation of arsenic rich solids from TMA, as indicated by the SEM-EDS data, e.g. Ni and Cr are much more effective than Mo or Fe. This suggests that chemisorption or compound formation involving TMA and Ni or Cr may also be important in causing the observed decrease in arsenic concentration with time. The interaction between TMA and the metal powders is being investigated by carrying out the SEM-EDS experiments in the absence of air. Sodium polysulfide has been shown to be an effective and inexpensive reagent for the removal organoarsines from natural gas.

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