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DETERMINATION OF TRACE NOBLE GASES IN AIR AND NATURAL GAS

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DETERMINATION OF TRACE NOBLE GASES IN AIR AND NATURAL GAS*

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ABSTRACT

A method was developed for the analysis of air and natural gas samples containing trace amounts of noble gases. The gas samples are preconcentrated by reaction with calcium at 900-1000°C and analyzed by mass spectrometry on an automated instrument. Methods of relating the concentrated sample to the original sample and the preparation of gas standards will be given. The accuracy of the technique at the 25 ppm level was determined. The precision of the method and requirements for improving the technique will also be discussed.

* This work was performed under the auspices of the U. S. Atomic Energy Commission.

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DETERMINATION OF TRACE NOBLE GASES IN AIR AND NATURAL GAS

INTRODUCTION

In the underground testing of nuclear devices in Nevada, He, Kr and Xe gases are added as tracers or are generated during the detonation. Gases, consisting principally of air, are pumped from the cavity to the surface and are sampled. For the last few years we have routinely analyzed these cavity gases* to determine the noble gas concentrations at the ppm level.

More recently we had a need to determine noble gases at the sub-ppm level in natural gas. This work resulted from the Lawrence Livermore Laboratory's effort to stimulate natural gas production with nuclear explosives. In the Rio Blanco event three nuclear devices were detonated simultaneously. Cylinders of Kr, Xe and Ne were emplaced with the lower, middle and upper devices, respectively. We had to determine the background of noble gases in gas samples from gas wells prior to the detonation and then analyze the post-shot gas samples quantitatively for the noble gas concentrations. From this data the Laboratory hoped to assess the extent of gas communication between the three cavities.

Ordinarily an analytical mass spectrometer can detect about 100 ppm of a component in a gas mixture. The most common method of lowering this detection limit in the case of samples containing noble gases is to remove the active gases by gettering them with hot calcium.[1] This method also eliminates interference from mass peaks due to the presence of active gases.

* These cavity samples are referred to as Nevada Test Site (NTS) samples throughout this paper to distinguish them from normal (atmospheric) air samples.

[1] Cady, G. H., and Cady, H. P., Ind. and Eng. Chem., Anal. Ed. 17, 760 (1945).

Horton[2] has used the gettering of air samples with titanium sponge to lower the detection limit. We have used both methods but found gettering with Ca faster than pumping with a titanium sublimation pump (TSP). H_2, CO_2 and hydrocarbons are pumped rather slowly by hot titanium. In the case of NTS samples gettering with Ca provides a 100-fold increase in the concentration of the noble gases. With natural gas samples the method typically gives a 10^4-fold increase in their concentration.

To calculate final results in ppm or ppb, the concentration factor* must be determined. For the NTS samples this is done using PVT measurements before and after removing the active gases from an aliquot with a TSP. In the case of natural gas samples, the percent of total gas pressure due to noble gases is found by analyzing the original sample, i.e. before concentration, on the mass spectrometer.

To calibrate the mass spectrometer, gas standards are prepared from normal air which has been gettered with Ca. The composition of normal air is obtained from literature values.[3] Pure gases are also used as standards.

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[2]Horton, J. C., Mass Spectrometric Analysis of Krypton and Xenon in Low Concentrations, Oak Ridge Gaseous Diffusion Plant, Rept. No. K-1843 (1973).

[3]Eck, C. F., J. Chem. Ed., 46, 706 (1969)

*Concentration factor = $\frac{\text{ppm total noble gases after gettering}}{\text{ppm total noble gases before gettering}}$

APPARATUS and PROCEDURE

Analysis of NTS Samples

The three steps in the analysis are:

a) the determination of percent noble gases in the original sample with a TSP using a small aliquot

b) concentrating the noble gases from about 800 cc_{STP} of sample gas by gettering active gases with hot calcium and

c) analyzing the concentrated sample by mass spectrometry.

The percent noble gases in the original NTS sample is determined with the apparatus shown in Figure 1. The pressure transducer is a CGS/Datametrics 10-torr Barocel.* The TSP with Ti-Mo filaments has a Varian Model No. 922-0032 power supply. The TSP was built at LLL to minimize the volume. It is cooled by water circulating in coils around the circumference of the pump. The sample bulbs are constructed of stainless steel and have a volume of approximately 800 cc. Fifteen grams of Ca shot are loaded into the bulb. A Nupro 8BK valve is attached to the sample bulb with Cajon 8VCR fittings.

The entire system exclusive of the sample cylinder is evacuated to about 10^{-6} torr. The sample bulb is filled to a pressure of about 1 atm. with sample gas and removed from the manifold. The determination of percent noble gases is made with the gas remaining in the vacuum cross. About 100 millitorr of gas is admitted to the manifold and 3-liter volume with the

*Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U. S. Atomic Energy Commission to the exclusion of others that may be suitable.

TSP valve closed. This initial pressure is recorded. Then the gas in the manifold and 3-liter volume is introduced into the TSP. The TSP filament is operated at 42 amps for one minute or less if a steady pressure value is attained. The final pressure is recorded and the percent of total noble gases in the sample calculated from the known volume ratio of the manifold and manifold plus TSP. The gas in the sample bulb is then gettered for 15 minutes at 900 to 1000°C with a resistance furnace of our design. The sample bulb is cooled and transferred to the mass spectrometry laboratory.

The mass spectrometer used for the gas analysis is a CEC Model 21-103C with a multiple, automated gas inlet system which can be operated under time-share control of a PDP-7 computer. To achieve a high sensitivity the ionizing current (electron collector current) is set to 70 microamps rather than the usual 30 microamps. Also, we use a sample pressure of about 300 millitorr in the expansion reservoir compared to about 50 millitorr used for routine gas analysis. The ion signal is detected with a Keithley Model 640 Vibrating Capacitor Electrometer with an input resistor of 2×10^{10} ohms. Then the signal is filtered with a 0.2 Hz active filter and amplified with a Hewlett-Packard Model 2470A Data Amplifier. A gain of 100 still gives a good signal-to-noise ratio. The effect of these operating conditions is to increase the mass spectrometer sensitivity (recorder divisions/millitorr) by a factor of about 200 over the usual sensitivity. At the same time the detection limit is lowered to about 1 ppm.

Samples are run on a routine basis in duplicate. Typically, a batch consists of two air standards and four air samples in duplicate.

Calculation of the results is performed with a program for the CDC-6600 computer. A typical computer output is shown in Table 1. Note that the difference between the observed and calculated pressures is listed to serve as an internal consistency test.

Natural Gas Analysis

The apparatus used to concentrate the natural gas samples is shown in Figure 2. Because the total concentration of noble gases may be only about 100 ppm, several aliquots (about 1500 torr-liter each) of gas must be concentrated before sufficient sample is available for analysis by the mass spectrometer. These aliquots are transferred from the concentrating chamber to the sample bulb by the English transfer pump and the Toepler pump. It is also possible to transfer samples which have been partially concentrated from the sample bulb back to the concentrating chamber for a final quantitative gettering.

Certainly it is very important to have the system free of vacuum leaks for this work. Of course, any atmospheric leak will contain 1% Ar. However, there is an internal check available to establish if vacuum leaks have occurred. The ratio of Ar^{40}/Ar^{36} for the natural gas samples differs from the same ratio for air; an examination of the consistency of these ratios is a valuable check on the integrity of the vacuum system.

While gettering the natural gas samples, the pressure is monitored with the pressure transducer. When the pressure reaches a constant minimum value, the oven is removed and the concentrator is allowed to cool to room temperature. This cooling is necessary in order to prevent the dissociation

of the various Ca compounds into Ca and the respective gases. For example, if the concentrator is not sufficiently cooled before the gas is transferred with the Toepler pump, large amounts of H_2 are observed.

After several aliquots of natural gas have been concentrated and transferred, the pressure in the sample bulb can be observed. It is seen from Figure 2 that the pressure transducer can be used to measure the pressure in almost any part of the system. This is very useful for leak checking, too. Volumes throughout the system have been minimized.

Results for the noble gas content in two different samples of natural gas are given in Table 2.

Detection Limits, Precision and Accuracy

The detection limits for the noble gases as a function of their original concentration are listed in Table 3. The second line corresponds to values for air samples; the third line represents a typical value for natural gas. Note that the first three lines are based on a sample pressure of 300 millitorr in the expansion reservoir and the fourth line refers to a pressure of about 30 millitorr. By concentrating more aliquots of the natural gas sample the detection limits are lowered as shown in Table 4.

The relative standard deviation (r.s.d.) for total noble gas concentration is less than ±1% on air standards gettered with a TSP. Four batches with a total of 18 normal air samples were gettered with hot calcium to evaluate the overall precision of this method, i.e. the precision value includes random errors due to the concentration and analysis steps. In Table 5 the r.s.d. values for the noble gases are listed. This precision

has been confirmed by over four years of experience in determining trace amounts of noble gases by this method. We routinely check the precision and reliability of our measurements by analyzing two air standards with each batch of samples. One air standard is assumed to be an "unknown" and its noble gas concentrations are calculated based on the other air standard.

The possible existence of systematic errors in the method was investigated by determining mass spectrometer sensitivities with pure noble gases and with the concentrated air standards. The sensitivities, so determined, typically agree to within ±1%, i.e. are within the precision of the method. In another accuracy check two mixtures of ^3He in argon were prepared and analyzed. The results are shown in Table 6. The agreement between calculated and experimental results was very good.

A check on the internal consistency of the mass spectrometric analyses is the agreement between the measured sample pressure in the expansion reservoir and the sum of the calculated partial pressures as shown in Table 2 on the computer printout. Typically, this pressure closure is within ±1%.

Method Improvement

Attempts to getter air samples on-line with the mass spectrometer were not successful because of insufficient cooling of the hot bulbs. This lack of rapid quenching resulted in N_2, O_2 and H_2 being dissociated from their respective compounds. Also, the ratio of the Kr/He peaks was not constant. However, a horizontally movable oven which can be quickly removed from the hot bulb and which is also amenable to remote operation has now been built.

Because the mass spectrometer is under computer control, it should be possible to automate the entire analysis. The additional time required for temperature equilibration could be gained by overnight runs. A program has already been written that automatically analyzes the concentrated gas samples. The determination of the percent of noble gases present could be accomplished by analyzing a sample of the original gas on the mass spectrometer rather than using the TSP. A synthetic mixture of noble gases could serve as a standard. Several bulbs could be heated by moving the furnace between them in the course of the analysis of several samples. An enlarged memory core on the time-shared computer should make possible the on-line calculation of the sample compositions.

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TABLES

FIGURES

TABLE 1. COMPUTER OUTPUT FORMAT

THIS IS SAMPLE NO. 3
POT 32-A (31813)

M/E	PPM BASED ON AIR STD	PPM DUE TO AIR
HE-3	.0005	
HE-4	5.2163	5.0330
NE	17.6313	17.4905
AR	8974.3960	8997.6963
KR	3.7884	1.0950
XE	.0787	.0836
TXE	.0831	.0836

PPM AR CALC BY DIFF - 8970.99
PPM INERTS BY ISP --- 8997.73
PPM AR CALC ON 36 PH IS 8974.40
SAMPLE PRESSURE IS 316.90 AND CALC PRESS IS 317.02
CLOSURE FOR SAMPLE IS -.12

TABLE 2. RESULTS FOR NOBLE GAS CONCENTRATIONS IN NATURAL GAS.

	LOCAL NATURAL GAS (PPM)	FAWN CREEK # 1 WELL (PPM)
He^4	440	80
Ne	-	< .015
Ar	100	11
Kr	.006	.001
Xe	.005	.001

TABLE 3. PPB DETECTABLE AS A FUNCTION OF TOTAL PPM OF NOBLE GASES

TOTAL INERTS (PPM)	CONC. FACTOR	PPB DETECTABLE				
		HE	NE	AR	KR	XE
10^6 (GROSS)	10^0	5,000	30,000	600	800	1,000
10^4	10^2	50	300	6.0	8.0	10.0
10^2	10^4	0.5	3.0	.06	.08	0.1
	BASED ON A 300μ SAMPLE PRESSURE					
10^2	10^4	5	30	0.6	0.8	1.0
	BASED ON A 30μ SAMPLE PRESSURE					

TABLE 4. PPB DETECTABLE KRYPTON VS. NO. OF ALIQUOTS CONCENTRATED

ALIQUOT NO.	PPM TOTAL INERTS	SAMPLE PRESSURE MASS SPEC (MILLITORR)	Kr^- DETECTABILITY IN PPB
1	90	22	.50
2	"	44	.25
3	"	66	.16
4	"	88	.13
5	"	110	.10
6	"	132	.08

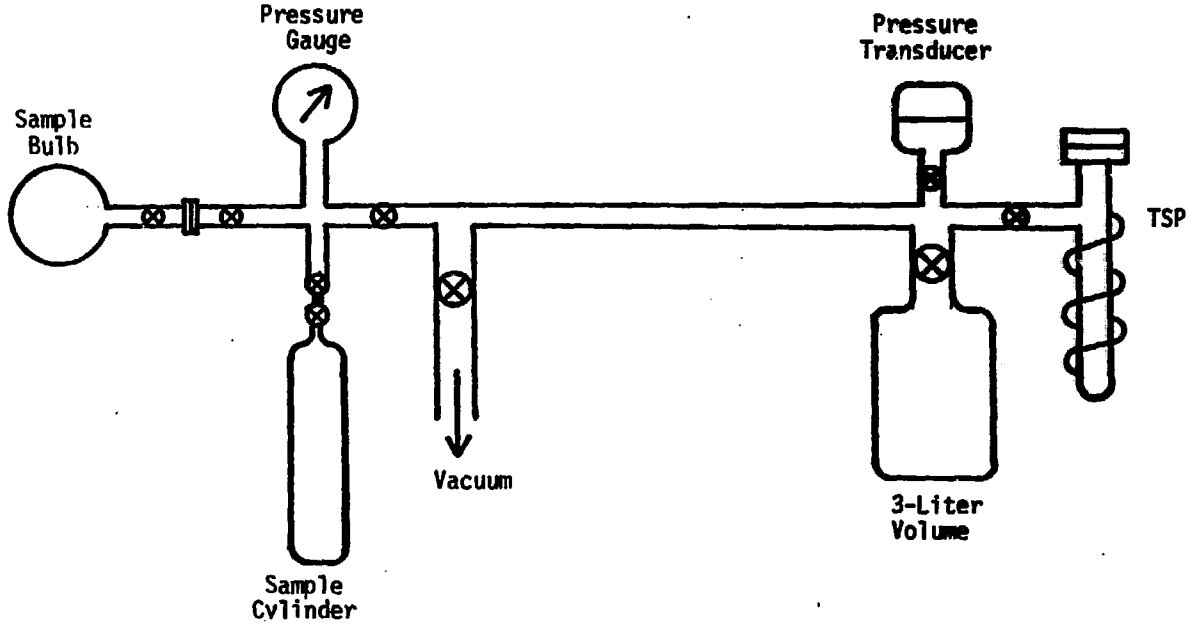
TABLE 5. RELATIVE STANDARD DEVIATION BASED ON ANALYSES OF CONCENTRATED AIR SAMPLES

	RELATIVE STD. DEV.	LEVEL IN AIR (PPM)*
HE	± 2%	5.24
NE	± 2%	18.21
AR	± 1%	9340.
KR	± 1%	1.14
XE	±15%	.087

* LITERATURE VALUE

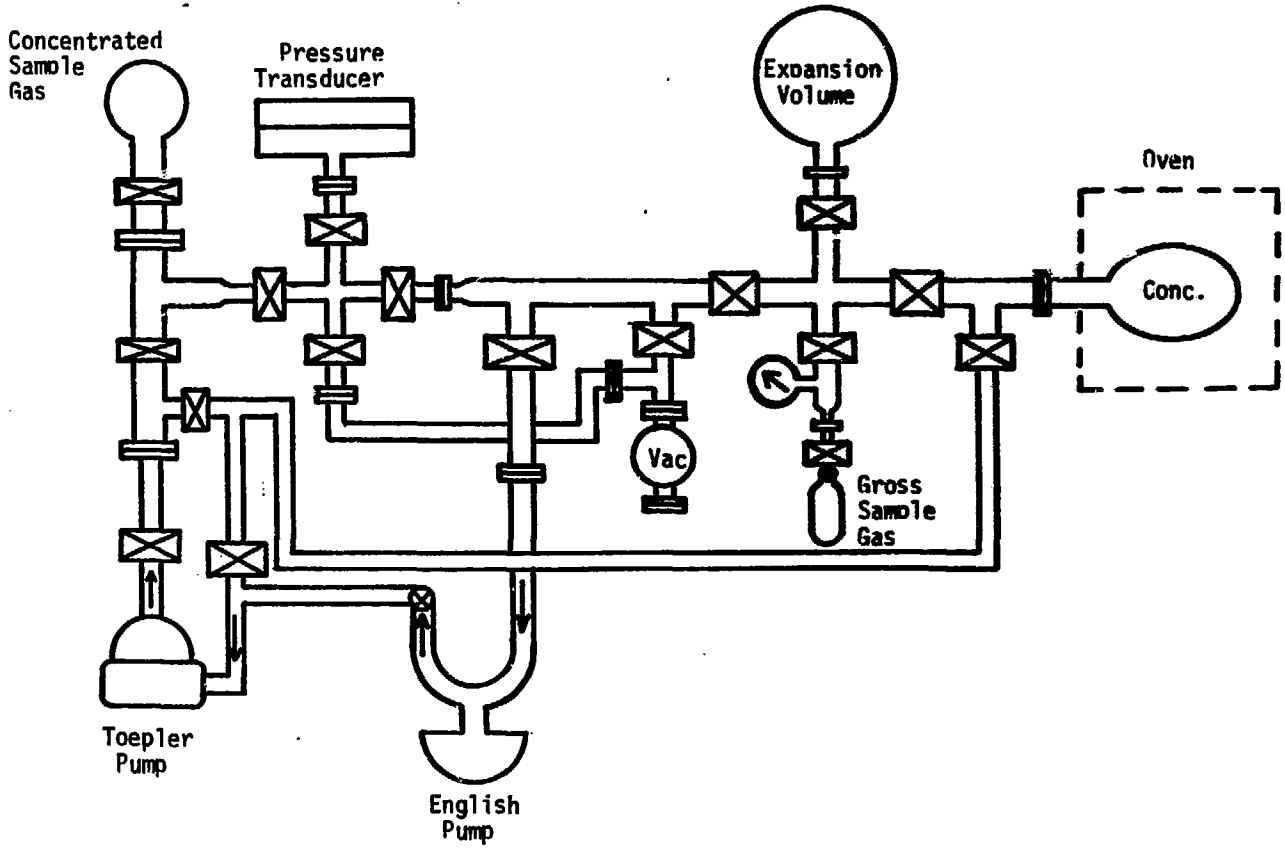
TABLE 6. ACCURACY OF He^3 AT 350 AND 25 PPM LEVELS

	STD. A	STD. B
CALCULATED PPM - He^3	350.	25.3
PPM DETERMINED - CONC. AIR STD.	352.	25.4
PPM DETERMINED - PURE GAS STD.	346.	25.0



Apparatus to Determine Percent of Noble Gases in Sample

Figure 1



Vacuum Line to Concentrate Natural Gas

Figure 2