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ISOTOPE CHROMATO-SPECTRAL ANALYSIS OF INORGANIC GASES

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SUMMARY

An isotope chromato-spectral method has been developed for the analysis of pure inorganic gases and their mixtures with the use of isotope dilution. The method permits to identify the main micro impurities (hydrogen, hydrocarbons, oxygen, nitrogen and their derivatives) with a high sensitivity and with a lower detection limit of 10^{-5} – 10^{-7} mole%. One of the main advantages of this method is the unnecessary of using standard mixtures. In this respect the method can be used for the estimation of standard samples of the pure gases and gas mixtures.

The analysis of pure inorganic gases is one of the most important problems in modern analytical chemistry. The main difficulty lies in the metrological support of the analysis, namely in the practical absence of standard samples of varying compositions of the analysed gases required for the majority of gas analytical methods. The creation of such patterns is a complicated task involving gas cleaning, quantitative and qualitative analysis of traces in mixtures and the prolonged storage of pure gases. Thus the necessity of creating methods which do not require such patterns arises.

One attempt to solve this problem is the usage of isotope dilution¹. The most promising method is a combination of this technique with spectroscopic measurements of the relative isotope concentration and a calculation of the unknown quantity of the analysed component is considered to be a long-term method. We have employed this principle in a method which uses a chromatographic separation combined with a preliminary cryogenic concentration step. The method allows us to define the main gas-forming elements, hydrogen, oxygen, nitrogen, carbon and sulphur, and also their compounds in inorganic gas mixtures and in pure gases.

In general the analysis procedure can be divided into the following stages: sampling of gas to be analysed; introduction of rare stable isotope of the analysed component; homogeneous distribution of isotope molecules in the resulting mixture, and its physico-chemical conversion; spectroscopic measurements of the relative isotope concentration and calculation of the amount of analysed component, C_x (mole-%), according to the formula (which is also true for the isotope dilution²)

$$C_x = \frac{[1 + (C_2/C_1)] [C_1/C_2 - (C_1/C_2)] P_1 V_1}{[1 + (C_1/C_2)] [1 - C_1/C_2(C_2/C_1)] P_2 V_2} \cdot 100$$

where (C_2/C_1) is the relative concentration of the rare and abundant isotopes of the analysed component as found naturally, (C_1/C_2) and C_1/C_2 the relative concentrations of the abundant and rare isotopes in the isotope gas and in the analytical mixture, respectively; P_1 , P_2 and V_1 , V_2 the pressure and volume ratios of the isotope and analysed gases, obtained as a result of manometric measurements of the isotope dilution process.

One of the first stages of the analytical procedure is the introduction into the gas sample of a rare isotope, which requires a set of calibrated cylinders and an accurate system of measuring the gas pressure therein. Thus the isotope is on the one hand an internal standard, which allows one to monitor the distortion of the gas composition at different stages of the analytical procedure, and on the other hand a measure of the unknown component, based on the relative isotope concentration in the resulting gas mixture.

The physico-chemical conversion of the analytical mixture is manifested in its cryogenic, adsorptional accumulation and subsequent chromatographic separation. The separation is conducted on packed columns with helium and argon as carrier gas at a velocity of 20–40 ml/min and decreased average gas pressure on the column. The use of a decreased pressure, $(2-3) \cdot 10^4$ Pa, creates optimum conditions for the light source, used as a differential detector, without changing the main parameters: separation efficiency, retention time and chromatographic peak width.

The separation of CO_2 and H_2O was performed on a glass column ($0.8 \text{ m} \times 5 \text{ mm}$ I.D.) packed with Porapak Q (50–80 mesh) at 273K, when the retention time of CO_2 was 1 min. Other mixtures of gases were separated on a glass column ($2 \text{ m} \times 5 \text{ mm}$ I.D.) packed with molecular sieve 5A (30–60 mesh), at 293 K. Under these conditions the retention time of hydrogen was 1 min and that of nitrogen was 5 min.

The cryogenic accumulation is of great importance as this stage largely defines the low limit for the analysis. The accumulation is conducted in special traps, packed with various sorbents and cooled to liquid nitrogen temperature, or in the chromatographic separation columns. For mixtures of H_2 , N_2 , CH_4 and CO , molecular sieves such as 5A, 13X or 10X were used in the concentrators; for CO_2 , Porapak Q was employed.

It is necessary to stress that the method described does not require the complete sorption or desorption of the isotope mixture during the concentration or chromatographic separation. It is important that isotopes should not be separated, *i.e.*, there should be no changes in the isotope composition of the analysed mixture. We have shown that in mixture of nitrogen in inert gases (He, Ne, Ar) concentrated on the molecular sieves 5A or 10X, at 77K for 10–50 min, there is no isotope separation. The same is true for the cryogenic concentration of CO_2 from He, Ne, Ar, N_2 or H_2 on Porapak Q.

The accumulation efficiency, A , defined the ratio of the quantity of component passed through the concentrator to that accumulated in it, depends strongly on the concentration of the component in the analysed gas. The dependence of A for nitrogen concentrated from helium on molecular sieves 5A (curve 1), 10X (curve 2, Fig. 1a), from neon on 5A and 10X (curve 1) and from argon on 5A and 13X (curve 2, Fig. 1b) and also of CO_2 from He, Ne, Ar, N_2 and H_2 on Porapak Q (curves 1–5, Fig. 1c) is shown. These results were obtained with the use of rare isotopes. The visible decrease in the accumulation efficiency at concentrations less than 10^{-3} – 10^{-4}

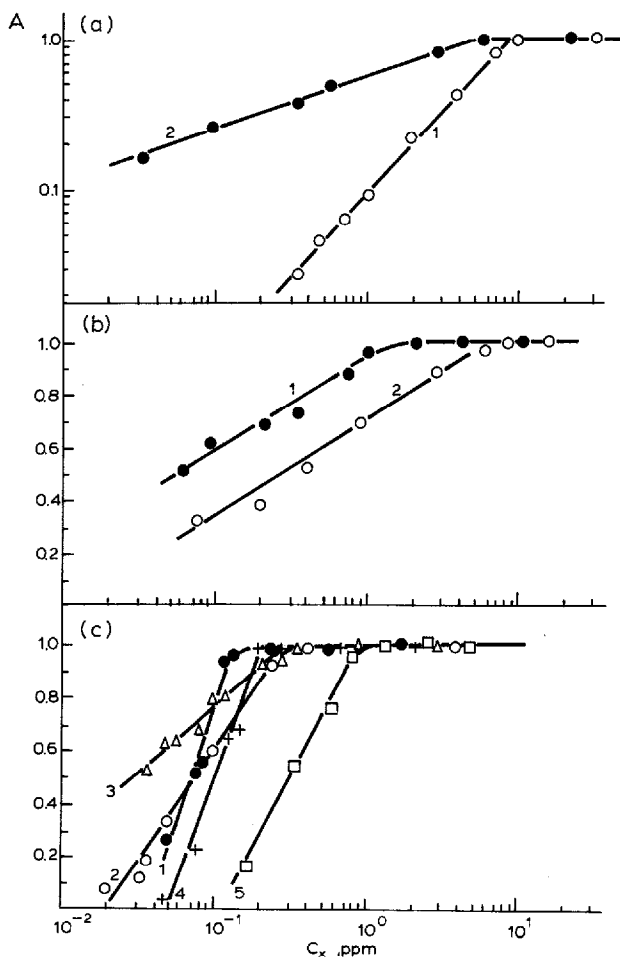


Fig. 1. The dependence of the accumulation efficiency, A , on the concentration, C_x (ppm), of various components concentrated on different sorbents at 77 K. For details see text. 1 = Helium; 2 = neon; 3 = argon; 4 = nitrogen; 5 = hydrogen.

mole% may be explained by the fact that under such conditions some molecules cannot reach the solid surface of the sorbent because of the low diffusion rate, and the others are too "hot" for the sorption process³. Apparently, without taking account of this decrease in the accumulation efficiency, systematic errors result from penetration of a part of the components in the concentrator. The suggested method allows to exclude the systematic error caused by this phenomenon.

The last stage of the analytical procedure is the spectroscopic definition of the isotope composition based on the direct relationship between the intensities of the spectral lines, radiated by the atoms or molecules, and their contents in the gas discharge plasma. For hydrogen, monoatomic lines of H (wavelength 481.6 nm, isotope shift 0.133 nm) are used for the analysis: for nitrogen, molecular lines (wavelength 380.5 nm, isotope shift 0.83 nm) and for oxygen and carbon, molecular lines

CO of the Angström system (wavelength 519.8 or 483 nm, isotope shifts 1.9 and 0.9 nm, respectively) are employed. These methods of isotope analysis for H, N, O and C are based on the use of the discharge at low pressure (0.13–13.3 kPa) and high frequency in a narrow quartz tube (2 mm in diameter, with external electrodes) as a light source. With such a light source, the determination of the isotope composition both in micro quantities of gases (10^{-1} – 10^{-4} ml) and in pure gases mixed with isotopes at levels of 10^{-1} – 10^{-3} mole% is possible.

In the study of this particular method special attention was paid to the accuracy and reproducibility of the results. Systematic errors were identified and taken into account at different stages of the analysis procedure: isotope effects in the light source and in the conversion block, "memory" effects, blank signals, etc. The validity of the method was demonstrated with some inorganic gases (Table I), and also by the use of a wide range of analysis conditions (Table II).

TABLE I
ANALYSIS OF SOME PURE INORGANIC GASES

Main component of mixture	Analysed gas	Amount (mole-%)	
		Introduced	Found
N ₂	He	$(6.21 \pm 0.08) \cdot 10^{-5}$	$(6.1 \pm 0.3) \cdot 10^{-5}$
		$(4.35 \pm 0.09) \cdot 10^{-6}$	$(4.4 \pm 0.5) \cdot 10^{-6}$
N ₂	Ne	$(3.52 \pm 0.04) \cdot 10^{-5}$	$(3.6 \pm 0.2) \cdot 10^{-5}$
		$(4.75 \pm 0.09) \cdot 10^{-6}$	$(4.7 \pm 0.3) \cdot 10^{-6}$
N ₂	Ar	$(2.45 \pm 0.03) \cdot 10^{-5}$	$(2.40 \pm 0.09) \cdot 10^{-5}$
		$(6.83 \pm 0.12) \cdot 10^{-6}$	$(6.9 \pm 0.4) \cdot 10^{-6}$
CO ₂	He	$(3.11 \pm 0.09) \cdot 10^{-5}$	$(3.2 \pm 0.1) \cdot 10^{-5}$
		$(6.03 \pm 0.05) \cdot 10^{-6}$	$(6.1 \pm 0.2) \cdot 10^{-6}$
CO ₂	Ar	$(2.50 \pm 0.05) \cdot 10^{-5}$	$(2.6 \pm 0.2) \cdot 10^{-5}$
		$(5.32 \pm 0.07) \cdot 10^{-6}$	$(5.3 \pm 0.2) \cdot 10^{-6}$
CO ₂	Ne	$(3.7 \pm 0.1) \cdot 10^{-5}$	$(3.5 \pm 0.3) \cdot 10^{-5}$
		$(7.2 \pm 0.2) \cdot 10^{-6}$	$(7.2 \pm 0.4) \cdot 10^{-6}$
CO ₂	N ₂	$(1.82 \pm 0.03) \cdot 10^{-5}$	$(1.8 \pm 0.2) \cdot 10^{-5}$
		$(5.06 \pm 0.04) \cdot 10^{-6}$	$(5.0 \pm 0.3) \cdot 10^{-6}$
CO ₂	H ₂	$(4.20 \pm 0.06) \cdot 10^{-5}$	$(4.4 \pm 0.3) \cdot 10^{-5}$
		$(6.31 \pm 0.11) \cdot 10^{-6}$	$(6.3 \pm 0.5) \cdot 10^{-6}$

The method described enables the analysis of both gas mixtures and pure gases⁴. For the latter, the method was used for the determination of traces of nitrogen and of hydrogen in the inert gases He, Ne and Ar, and also for the determination of carbon dioxide in N₂, H₂, He, Ne and Ar. The limits of the determination of such components are 10^{-7} – 10^{-5} mole% depending on the random errors.

TABLE II
CONDITIONS FOR THE ANALYSIS OF SOME INORGANIC GASES

Main component of mixture	Introduced gas (mole% · 10 ⁵)	Parameters varied			Amount found, C _x (mole% · 10 ⁵)
		ω_p (ml/min)	τ_p (min)	Carrier gas	
He	N ₂ 6.21 ± 0.08	100	5	He	6.2 ± 0.3
		250	4	He	6.0 ± 0.3
		500	4	He	6.1 ± 0.3
He	CO ₂ 3.11 ± 0.09	400	5	He	3.0 ± 0.1
		600	10	He	3.2 ± 0.1
		800	15	He	3.1 ± 0.1
Ne	N ₂ 3.52 ± 0.04	250	20	He	3.5 ± 0.1
		600	10	Ne	3.6 ± 0.1
		300	50	Ne	3.6 ± 0.1
Ne	CO ₂ 3.7 ± 0.1	300	5	He	3.5 ± 0.3
		500	10	He	3.8 ± 0.3
		800	15	He	3.6 ± 0.3
Ar	N ₂ 2.45 ± 0.03	670	15	He	2.4 ± 0.1
		800	10	He	2.5 ± 0.1
		500	20	Ar	2.4 ± 0.1
Ar	CO ₂ 2.50 ± 0.05	500	10	He	2.6 ± 0.2
		300	15	He	2.7 ± 0.2
		100	30	He	2.3 ± 0.2
N ₂	CO ₂ 1.82 ± 0.03	300	20	He	1.7 ± 0.2
		500	15	He	1.8 ± 0.2
		800	10	He	1.8 ± 0.2
H ₂	CO ₂ 4.20 ± 0.06	700	15	He	4.6 ± 0.5
		450	10	He	4.4 ± 0.5
		200	5	He	4.0 ± 0.5

ω_p , τ_p = velocity and time of pumping of the analytical mixture through the concentrator.

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