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PRACTICAL METHOD FOR THE PURIFICATION OF CARRIER GASES FOR GAS CHROMATOGRAPHY

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SUMMARY

For sensitive analysis of traces of inorganic gases, detectors are employed based on Penning's effect, which requires pure helium or neon as the carrier gas. These gases may be purified by an electric discharge. This method is based on cataphoresis, *i.e.* the change in composition of a gaseous mixture in an electric field. This change is the result of a flow of contaminant ions and is important when the ionization energy of the contaminant gas is lower than the energy of a metastable level of the carrier gas. The positive ions flow towards the cathode, which is compensated for, in the closed vessel, by a diffusive flow of neutral particles. If the electrodes are hollow and used as gas exit from the chamber, the compensating flow of neutral particles will decrease and the concentration of the contaminant in gas flowing out of the chamber through the cathode will increase. Accordingly, the concentration of the contaminant in gas flowing away through the anode becomes lower than the initial concentration. Construction of the discharge chamber and the value of the electric current depend on the initial concentration of the contaminant and the required level of purity. The experimental results show that the method may be used for the complete purification of helium and neon with low initial concentrations of contaminant. In this case, total ionization and purification can simply be obtained by a corona discharge.

INTRODUCTION

Methods of microcontaminant analysis based on the Pennings effect in the self-maintained discharge[1] and radioionization detection methods[2] are widespread. These methods imply the use of carrier gases with high ionization energies and excitation energies of a metastable type. Helium and neon are the best gases for this purpose. The use of these gases make it possible to determine microcontaminants having volume fractions of 10^{-8}–10^{-7}. In this case the bottled carrier gases must be purified.

Devices for purification of rare gases should meet a number of requirements, the main ones being that they can be employed directly before the gas enters the chromatograph and simplicity of realization. The absence of a regeneration cycle is also desirable. All the known methods of purification (catalytic, low temperature adsorptive, etc.) do not meet all these requirements.

The purpose of the present work was to develop a method of purification of the rare gases used for highly sensitive chromatographic analysis.

EXPERIMENTAL

It is suggested that use should be made of cataphoresis. It is known[3,4] that if an electric discharge is obtained in the tube containing a gas with an high ionization potential, *e.g.,* helium, and a low contamination of a gas with a lower ionization potential, the concentration of the latter will decrease at the anode and increase at the cathode. As a rule, cataphoresis takes place in closed discharge tubes at pressures of 10^3–10^4 Pa in the glow discharge mode.

In this work cataphoresis has been used for the purification of the helium at positive pressures. Fig. 1 shows the discharge chamber used. Gas enters the chamber through inlet pipe union 1. Inside the chamber are hollow electrodes 2 and 3, which are connected with pipe unions 4 and 5 used for evacuating the gas from the chamber. A d.c. voltage applied to the electrodes provides a stable discharge. Discharge in the chamber took place at the support points on the edges of the hollow electrodes, thereby creating a discharge column between them. Under such conditions the amount of contaminant in helium flowing out of the chamber through the cathode increases at the expense of a drift of positive ions towards the cathode. The amount of contaminant in helium flowing out through the anode decreases since there is no flow of positive ions to the anode. In the presence of electronegative components a flow of negative ions towards the anode is formed.

The helium in the chamber has a total contaminant volume fraction of less than $5 \cdot 10^{-5}$. The main contaminants are neon, hydrogen, nitrogen, oxygen and carbon monoxide. The volume fraction of neon was about 10^{-5}, those of the other components were 10^{-6}.

DIAGNOSTICS

The current–voltage characteristics, potential gradients on the discharge column and radiation spectra were measured in order to investigate the discharge plasma composition and estimate the possibilities for cataphoresis.
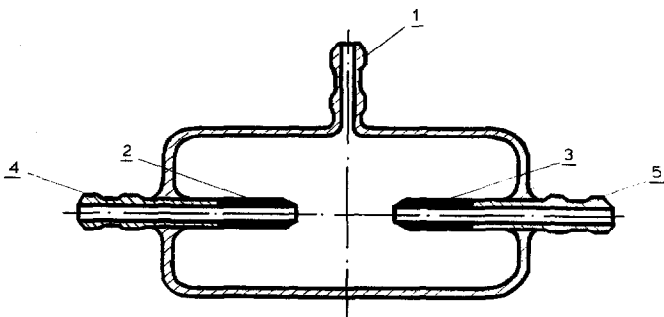

Fig. 1. Discharge chamber for rare gas purification: 1 = inlet pipe union; 2, 3 = hollow electrodes; 4, 5 = pipe unions for gas evacuation.

At low currents the discharge has a diffusive form and the discharge voltage is constant. At certain values of the current, depending on the pressure in the chamber and contaminant concentration, the discharge contracts and the voltage decreases. The current–voltage characteristics of the discharge obtained for a gap of 12 mm at a pressure of 0.18 MPa in the chamber and at a rate of gas flow through the electrodes of 20 ml/min is shown in Fig. 2. Contraction takes place at a current of 0.5 mA. The potential gradient on the discharge column is about 200–400 V/cm.

The emission spectra of a contractive discharge at a current of 3 mA and a pressure of 0.18 MPa without a gas flowing through the electrodes was recorded in order to make a qualitative estimation of the plasma composition. In the central part of the discharge there is a superposition of a line emission spectrum and an intensive continuous spectrum. The emitted lines are of helium, hydrogen, iron, the latter being a component of the electrode material. In the outside part of the discharge, the continuous spectrum is essentially absent and the spectral lines are due to helium and hydrogen. Under the same discharge conditions, the emission spectrum of helium containing 2% hydrogen exhibits spectral lines due to molecular hydrogen as well as to atomic H and He, but not to iron. In both cases, spectral lines due to atomic N, O, Ar and Ne were not obtaied.

The electron concentration as measured by the Stark broadening of spectral line H_β in the central part of the discharge is $2.1 \cdot 10^{15}$ cm^{-3} for bottled helium and $6.1 \cdot 10^{15}$ cm^{-3} for the mixture with 2% hydrogen.

ANALYSIS

The extent of purification of helium in the discharge, that is the cataphoresis efficiency, was estimated by analysis of the gas flowing out through the anode and cathode. A method of adsorptive concentration of impurities followed by analysis on a Tsvet-100 chromatograph was used[5]. The initial volume fraction of nitrogen was found to be $2 \cdot 10^{-6}$ and was the same in both flows exiting from the chamber. Argon and oxygen were not measured because they form ions of opposite signs.
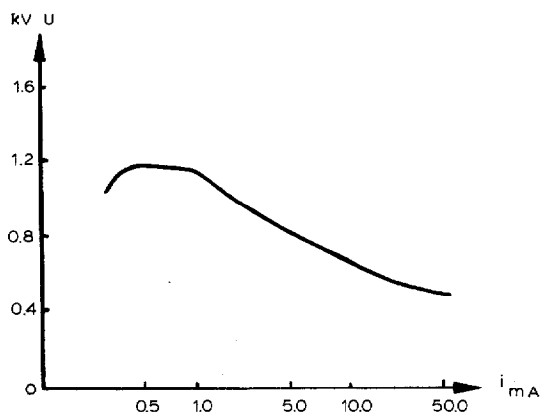

Fig. 2. Current–voltage characteristics of the discharge.

RESULTS

   During the discharge, the concentration of nitrogen in the helium flowing out through the cathode increases, but decreases in the flow out through the anode. At a pressure of 0.18 MPa in the chamber, a discharge current of 3 mA caused the nitrogen concentration to vary by 20%. An increase in the discharge current to 100 mA resulted in a doubling of the cataphoresis efficiency, moreover the same variation in the nitrogen concentration flowing out through the different electrodes was observed. With a further increase in the discharge current, the increase in nitrogen concentration in the gas flowing out through the cathode did not correspond to the decrease in concentration in the gas flowing out through the anode.

   Chromatograms of the gas flowing out of the chamber are shown in Fig. 3. Fig. 3a shows that for no discharge, Fig. 3b shows that for a discharge current of 1 A and gas flowing out through the anode and Fig. 3c shows that for a discharge current of 1 A and gas flowing out through the cathode. The pressure in the chamber was $1.3 \cdot 10^5$ Pa, the flow-rate of gas was 30 ml/min. It is seen that there is a variation in the nitrogen concentration in the helium flowing out through the anode and cathode.
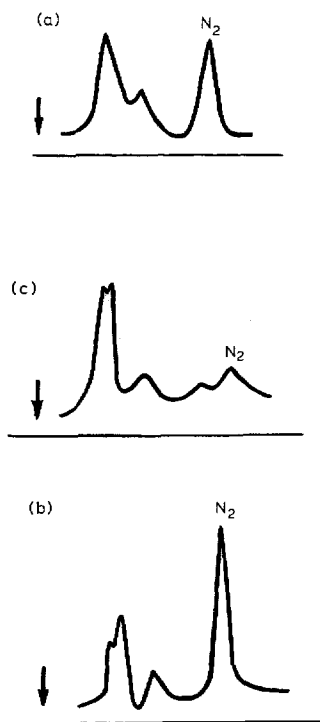

Fig. 3. Chromatograms of the gas flowing out of the discharge chamber: (a) no discharge; (b) discharge current 1 A, gas flowing out through the anode; (c) discharge current 1 A, gas flowing out through the cathode.

A decrease in the nitrogen concentration by a factor of 7–10 was obtained at a discharge current of about 1 A. In these experiments a forced cooling of the electrodes and discharge chamber was used.

DISCUSSION AND CONCLUSIONS

The main problem in the application of cathaphoresis for the purification of helium is to provide a sufficient ionization of the gaseous contaminants in the discharge column. In order to obtain a complete removal of the contaminants, all of their atoms and molecules must be ionized. If the total content of contaminants is known, then considering all ions in the discharge to be due to the contaminants it is possible to estimate the lowest current necessary for their complete ionization. However, these estimations are not realistic since the spectroscopic investigations show an important rôle of helium and of the electrode material in the discharge. Especially relevant are the atoms of iron appearing in the discharge as a result of electrode erosion. As iron has a lower ionization potential than the contaminants and helium, it decreases the electron temperature of the plasma and the concentration of contaminant ions. In order to increase the latter it is necessary to increase the current, thus intensifying the electrode erosion and loss of metal vapour into the discharge space. An estimation of the electron concentration according to the Stark broadening of the spectral line H_β has shown that the presence of a component such as iron in the contracted discharge affects the degree of ionization, which can reach 10^{-4} even at a current of 3 mA. Under such conditions an active ionization both of iron and the contaminant takes place, leading to the cataphoresis process. The ionic composition and characteristics of the plasma are not entirely dependent on the electrode material, as is clear from the experiments with a mixture of helium and 2% hydrogen, where spectral lines due to iron were not found and the electron concentration is increased three-fold.

The increase in the nitrogen concentration in the gas flowing out through the cathode approximately determines the degree of ionization of nitrogen in the discharge. One can also estimate the fraction of nitrogen ions at a current of 3 mA to be 10^{-2}.

Erosion of the electrode material leads to another effect that influences the cataphoresis, i.e., adsorption of gaseous contaminants by the vapours of the electrode material. This effect is clearly seen at currents > 1 A.

Thus, the experiments have demonstrated the possibility of purifying helium in the gas discharge plasma at a high pressure, and some qualitative characteristics of the process have been obtained. The method described can be used when the initial concentration of contaminants is sufficiently low. In this case, it is possible to have low discharge currents which do not cause a considerable erosion of the electrodes. The degree of purification obtained is greater the lower is the initial content of contaminants. This shows that the method can be used for highly sensitive chromatographic analysis.

REFERENCES

1 J. E. Lovelock, *Nature (London)*, 181 (1958) 1461.
2 V. A. Rotin, *Radioionizatsionnoe Detektirovanie*, Atomizdat, Moscow, 1974, p. 188.
3 M. Druyvestein, *Physica*, 2 (1935) 255.
4 L. M. Chanin, *Gaseous Electronics*, Vol. 1, Academic Press, New York, 1980, p. 133.
5 A. A. Zhukhovitskyi and N. I. Turkeltaub, *Gazovaia Khromatografia*, Gostoptehizdat, Moscow, 1962,
  p. 442.