

Evaluation of a pulse-discharge helium ionisation detector for the determination of neon concentrations by gas chromatography

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Abstract

A pulse-discharge helium ionisation detector, PDHID (Valco, PD-D2-I) with sample introduced to the discharge zone is shown to be applicable for reliable determinations of neon by gas chromatography. The detection level of 80 pg was obtained, but the dependence between detector response and neon mass was non-linear. However, for the discharge gas doped with 33 ppm of neon, a linear response to the neon mass up to 10^{-5} g and the detection level of 0.5 ng were obtained. The method can be used for measuring neon concentrations in groundwater systems for hydrogeological purposes.

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1. Introduction

Neon analyses by gas chromatography were possible in the past only with the aid of thermal conductivity detector with a poor detection level. On the other hand, a helium detector, equipped with radioactive source, can be used for detection of all compounds except of neon. The response in that kind of detector is achieved by ionisation of analysed molecules in interaction with helium atoms excited to metastable states [1,2]. The neon atom having ionisation potential of 21.6 eV cannot be ionised in collision with metastable helium atom excited to 19.8 eV. Therefore, neon should theoretically not be detected by such detector. However, in a pulse-discharge helium ionisation detector (PDHID), developed by Wentworth et al. [3,4], a small response for neon is observed. In that detector, helium is ionised by high voltage pulse discharge between two electrodes. The part of a detector in which the discharge occurs is called the discharge zone. Helium flowing through the discharge zone transports excited helium atoms to another part of the detector, called the reaction zone. Analysed sample molecules introduced with the carrier gas (helium) into the reaction zone interact with excited helium atoms

and influence the detector ionisation current measured by an external control unit (CU).

In an earlier paper, the application of the PDHID for measurements of neon concentrations in air and water were presented [5]. The discharge gas (helium) flowed through the discharge zone whereas the carrier gas (also helium), and samples were introduced to the reaction zone according to the producer's recommendation (Valco Inc.). The detector response was not linear for neon, however, by introduction of trace amounts of neon into the discharge gas yielded a linear characteristic for neon mass up to 10^{-6} g. The detection level was 1.8 ng.

Wentworth et al. [4] suggested that the response of a PDHID for permanent gases can be increased by a factor of 5–10 if the sample is directly introduced to the discharge zone. Following that idea and contrary to the producer's recommendation, a commercially available PDHID was tested within the present work for measuring of neon in samples introduced into the discharge zone.

2. Experimental

2.1. Description of the measurement system

The measuring system used within this work is shown in Fig. 1. The system consists of the PD-D2-I detector, two

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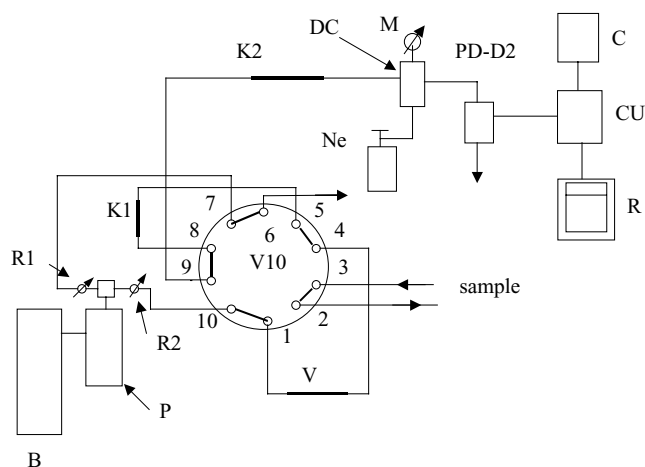


Fig. 1. Scheme of the measurement system (description in the text).

chromatographic columns (K1 and K2) and a 10-way Valco valve (V10). Helium of 99.9999% purity (Linde) from a bottle (B) was additionally purified with the aid of the Valco HP2 purifier (P in Fig. 1). The carrier gas, helium, regulated by regulator R2, supplies the discharge zone of the detector. Helium regulated by regulator R1 is also used for cleaning the column K1, when it works in the “back flush” mode. The valve V10 is equipped with a sample loop (V) and is connected with the columns K1 and K2 filled with molecular sieve 5A. The diameter of the columns is 2 mm and their lengths are 1.5 and 3 m, respectively. The analysed sample is introduced to points 2 and 3 of the 10-way valve. The columns K1 and K2 operate in a “back flush” mode. After filling the sample loop with analysed air and switching the valve V10, the sample is injected into the column K1 connected with the column K2. In the column K1 sample compounds are partly separated. Neon and hydrogen are first eluted from the column K1. When these gases are in the column K2, the valve V10 is switched again. In that state, neon and hydrogen are separated in the column K2, whereas helium from the regulator R1 flows in reverse direction in the column K1 to remove all remaining gases.

The discharge zone of the detector was supplied with clean helium or with helium doped with neon, which was introduced to helium in a diffusion chamber (DC in Fig. 1) inserted between the end of the column K2 and the detector when doping was used.

The PDHID system is equipped with a pulse generator and a control unit. A computer (C) with the SRI-PeakSimple program was used for data collection, and a recorder (R) to observe chromatograms.

2.2. A detector response for sample introduced to the discharge zone of the detector

The comparison of detector responses for neon when sample is introduced to the discharge and reaction zones is shown in Fig. 2. The different neon masses were obtained

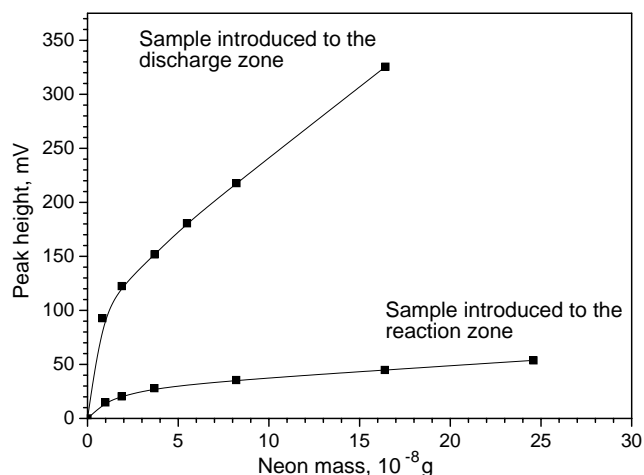


Fig. 2. Comparisons of detector responses for samples introduced to the discharge or reaction zone.

by injection of air samples containing 18.18 ppm (about $1.6 \cdot 10^{-8}$ g/cm³ STP) of neon with sample loop volumes varied from 0.6 to 15 cm³. The injection of such large air samples was possible because only neon and hydrogen were allowed to pass through the column K2 and the detector after separation in the column K1. It can be seen in Fig. 2 that the introduction sample to the discharge zone increase detector response. For both methods of sample introduction to the detector, the responses are not linear but positive. The positive response means that neon causes an increase of the detector ionisation current.

2.3. Influence of neon doping on detector characteristics

The influence of neon doping on detector characteristics was investigated using the same diffusion chamber as that used in [5]. The diffusion chamber was placed between the end of column K2 and the detector (Fig. 1). The influence of neon pressure in the diffusion chamber on neon concentrations in helium flowing with flow rate of 24 cm³/min through the capillary inserted in the chamber is shown in Fig. 3. For the neon pressure in the chamber higher than about 1 bar, the dependence is linear.

The detector characteristics for 33 ppm of neon in the discharge gas and without doping are shown in Fig. 4. A wide range of analysed neon mass was obtained by using the exponential dilution method. It can be seen that the application of the neon doping makes the detector characteristic linear for analysed neon masses up to 10^{-5} g. It is worth mentioning that for high masses of analysed neon, the response of the doped detector becomes larger than that of non-doped.

The detector characteristics for different concentrations of doping neon and for both systems of sample introduction to the detector are shown in Fig. 5. It can be seen that an increase of the concentration of doping neon decreases the slope of the detector characteristics and causes a decrease of the detection sensitivity. The highest detection

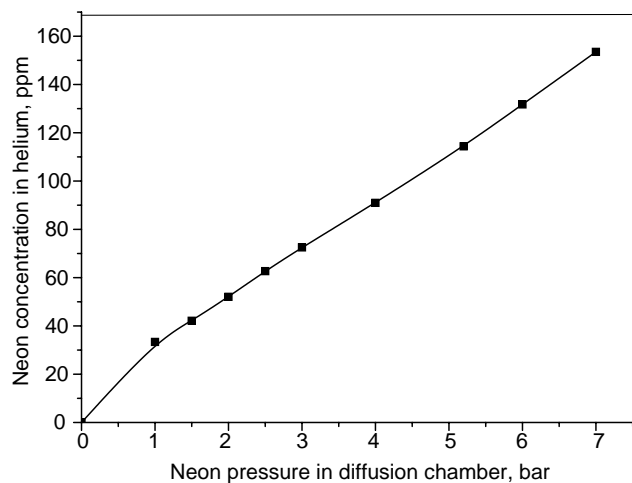


Fig. 3. Neon concentration in helium vs. neon pressure in the diffusion chamber for 30 cm³/min of helium flow rate.

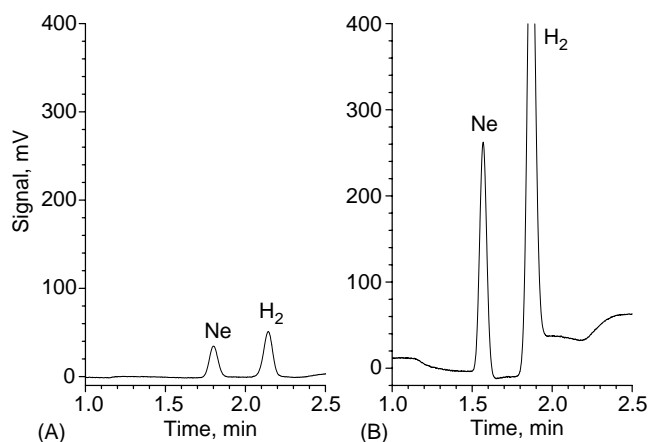


Fig. 6. Examples of neon analysis of 10 cm³ of air injected to the: (A) sample introduced to the reaction zone, (B) to the discharge zone.

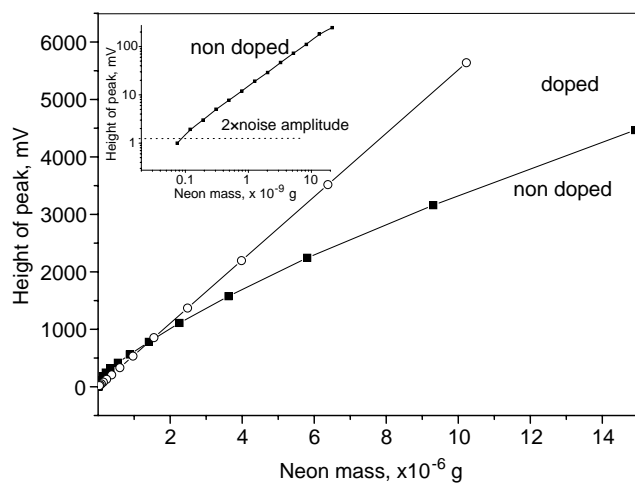


Fig. 4. The influence of doped and non-doped discharge gas on the detector characteristics for samples introduced to the discharge zone.

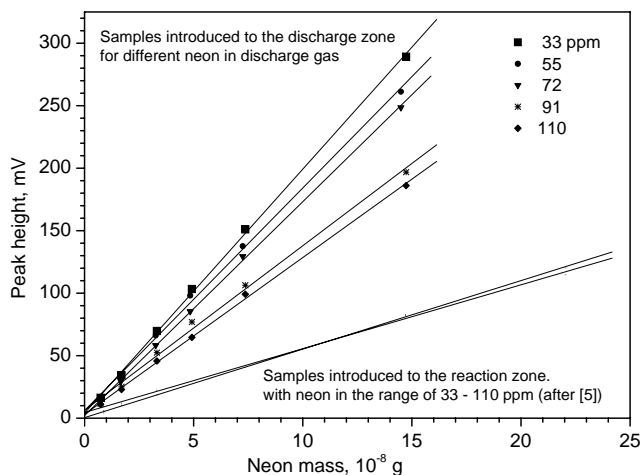


Fig. 5. Comparison of the detector characteristics for different neon concentration in the discharge gas for samples injected to the discharge and reaction zones.

sensitivity was obtained for the doping neon concentration of 33 ppm.

When samples were introduced into the discharge zone of a PDHID, detection level of 80 pg was obtained, but the detector characteristic was non-linear. For the detector doped with 33 ppm of neon, the detection level was only about 0.5 ng, but its characteristic was linear up to neon mass of 10⁻⁵ g. Examples of 10 cm³-air sample analysis are shown in Fig. 6 for samples introduced to the reaction (A) and discharge zones (B).

3. Mechanism of doping

Physical mechanism responsible for the detector signal generation for neon remains unclear, particularly when samples are introduced to the reaction zone. In that zone, excited helium dimmers emit radiation in the energy range from 17.86 to 19.7 eV [3] whereas ionisation of neon requires the minimum photon energy of 21.56 eV. In spite of that, the neon signal is positive, which indicates that some ionisation of neon occurs. Within the present work, improved sensitivity is obtained for neon samples introduced into the discharge zone, both without doping and with doping. That better sensitivity is probably related to direct ionisation of neon atoms by electrons generated in the discharge zone.

The influence of the neon doping on the shape of the detector characteristics can be explained as follows. The non-doped detector characteristic shown in Fig. 7 (dotted line) consists of two parts. The first part is non-linear up to neon mass of 3 · 10⁻⁸ g, and the second part is linear above that mass. Additional introduction of a constant flux of neon into the discharge gas (33 ppm which corresponds to about 3 · 10⁻⁸ g/cm³ in the discharge gas) moves the zero point (point A in Fig. 7) to the linear part of the characteristic (point B in Fig. 7), and the detector works in the linear range of the characteristic.

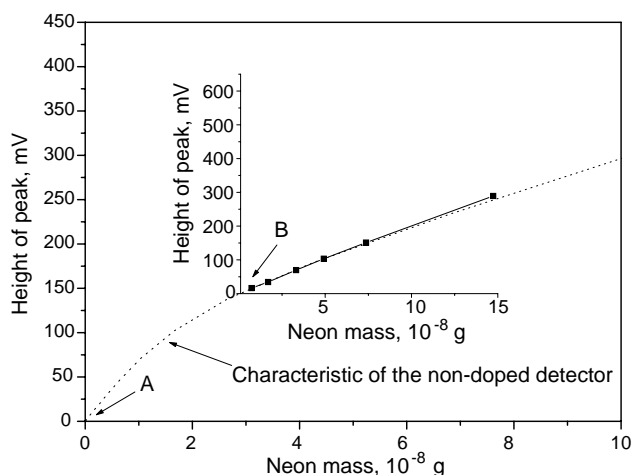


Fig. 7. Position of the detector characteristic with doping on that without doping.

4. Conclusions

In the previous study, the PDHID, with sample introduced to the reaction zone and doped with neon, was shown to be applicable for measurements of neon concentration in air and after enrichment also in groundwater [5]. Within the present work it has been shown that the response for neon can be greatly improved for the PDHID with samples introduced to the discharge zone and the discharge gas doped with neon. The detection level is then about 0.5 ng, which for the gas

sample volume of 10 cm^3 corresponds to the concentration of $2.2 \cdot 10^{-11} \text{ g/cm}^3$.

For such detection level, it is possible to measure neon concentrations in groundwater without sample enrichment. For instance, measurements of neon concentrations in groundwater with the aid of the PDHID, together with argon measurements [6], were used for determining the recharge temperature and “excess air” in a groundwater system [7].

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