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Short communication

## Application of a pulse-discharge helium detector to the determination of neon in air and water

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### Abstract

A pulse-discharge helium detector (Valco, PD-D2-I) is used to measure neon concentrations in air and water. The detection level is  $0.5 \times 10^{-8}$  g/cm<sup>3</sup> (0.2 ppm). Discharge gas doped with neon results in a linear response to the neon mass up to  $10^{-6}$  g. For measuring the neon concentration in water, a simple enrichment system is used.

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### 1. Introduction

Measurements of noble gases in groundwater are needed for determining the noble gas temperatures, i.e. the temperature at which water was recharged to the groundwater system [1]. Noble gas measurements are also needed for determining the so-called “excess air” [2,3] in order to correct measured concentration of freons and SF<sub>6</sub> used for groundwater dating [4]. The noble gas concentrations are usually measured by costly mass-spectrometric methods. Therefore, the application of much cheaper gas chromatography (GC) methods is of interest.

First attempts to measure neon concentrations in water by gas chromatography were reported by Sugisaki and Taki [5] who used oxygen as a carrier gas and a TCD detector. Attempts to use helium-discharge photoionisation detection (HDPID,

Hitachi) for measurements of noble gases were presented by Ogino and Amura [6]. For measuring the neon concentration, the discharge gas was doped with neon, which resulted in a sixfold increase of the detector signal yielding the detection level of 0.2 ppm. Pulse-discharge helium ionisation detection (PDHID, Valco) can be used to measure neon at similar detection level without doping [7]. In the above-mentioned detection methods both the discharge gas and sample flow through the discharge zone.

Within the present work a PDHID system, type PD-D2-I, was used for the detection of neon. In this detector type, the discharge gas flows through the discharge zone whereas the carrier gas and sample are introduced into another zone of the detector [8].

### 2. Experimental

#### 2.1. Description of the measurement system

The measuring system used within this work is

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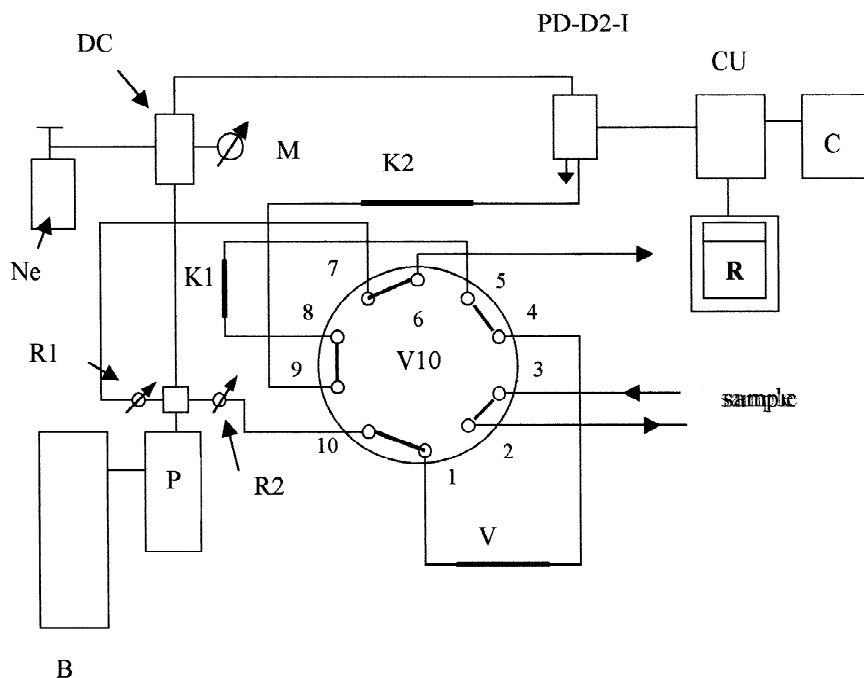


Fig. 1. Scheme of the measurement system (description in the text).

shown in Fig. 1. The system consists of the PD-D2-I detector, two chromatographic columns (K1 and K2) and a 10-way Valco valve (V10). Linde helium of 99.9999% purity from bottle (B) was additionally purified by a Valco HP2 purifier (P in Fig. 1). Helium supplies the detector discharge zone and is also used as a carrier gas, which is regulated by two regulators R1 and R2. The valve V10 is equipped with a sample loop (V) and is connected with 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 samples were introduced to points 2 and 3 of the 10-way valve. Columns K1 and K2 operate in the “back flush” mode. After filling the sample loop with analysed air and switching the valve V10, sample is injected into the column K1 connected with column K2. In the column K1 sample compounds are partly separated. Hydrogen and neon are first eluted from the column K1. When these gases are in the column K2, the valve V10 is switched

again. In that state, hydrogen and neon are separated in the column K2, whereas the carrier gas flow is reversed in the column K1 to remove all remaining gases.

The PDHID system is equipped with a pulse generator and a controller unit (CU). According to the manufacturer’s instructions, the ionisation current of the detector, displayed in the controller unit, should be in the range from 0.5 to 1.5 nA to monitor the proper work of the system. A computer (C) with the SRI-PeakSimple program was used for data collection, and a recorder (R) to observe chromatograms.

The discharge zone of the PD-D2-I detector was supplied with either helium or helium with trace amounts of doping gas. The doping gas was introduced to helium in a diffusion chamber (DC in Fig. 1) similar to that used in the Fractovap G.H. chromatograph produced by Carlo Erba (Italy). This chamber was equipped with a 7-cm-long PTFE capillary tube of 2 mm outside and 1 mm inside

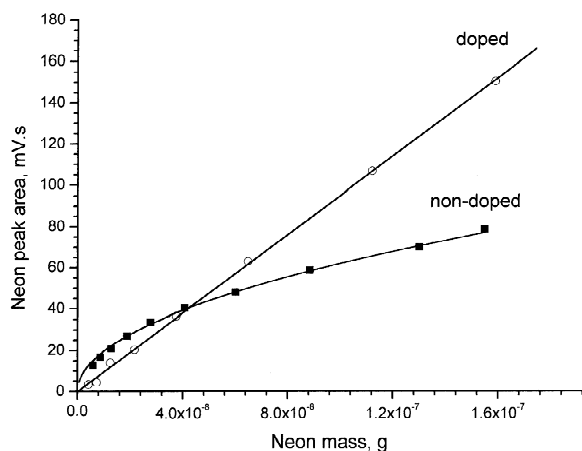


Fig. 2. The influences of doped and non-doped discharge gas on the detector characteristics.

diameter. The quantity of neon doping gas in helium was regulated by pressure in the diffusion chamber with a manometer (M).

2.2. Influence of neon doping on detector characteristics

Air samples of different volumes injected into the

measuring system showed that the detector response is not linear for neon and linear for hydrogen. The influence of the doping gas on the characteristics of radioionisation detectors was investigated in earlier works by injecting into carrier helium small amounts of hydrogen [9–11] or neon [6]. For the PD-D2-I detector, the use of hydrogen as a doping gas resulted in an increase of the detector current, which was, however, unstable. On the other hand, the use of neon as a doping gas yielded a linear characteristic though without better detection level as shown in Fig. 2. Both with doping and without doping, the detection level of neon for the PD-D2-I detector is estimated at  $0.5 \times 10^{-8} \text{ g/cm}^3$  (0.2 ppm).

Samples containing large masses of neon were injected into the chromatographic system by means of the exponential dilution method to check the linearity. The detector characteristics are linear up to  $10^{-6} \text{ g}$ , for different pressures of neon in the diffusion chamber, as shown in Fig. 3.

2.3. Determination of neon concentration in water

Neon was separated from a water sample in a 2600-cm<sup>3</sup> glass vessel by the head space method [12]. The head-space created in the vessel was filled with nitrogen of 6.0 purity (99.9999%). After several minutes of shaking, 10-cm<sup>3</sup> head-space gas were

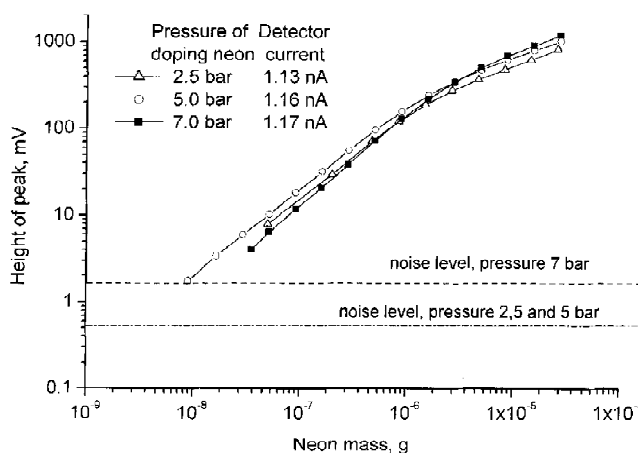


Fig. 3. The dependence of the linear range of the detector response on neon pressure in the diffusion chamber.

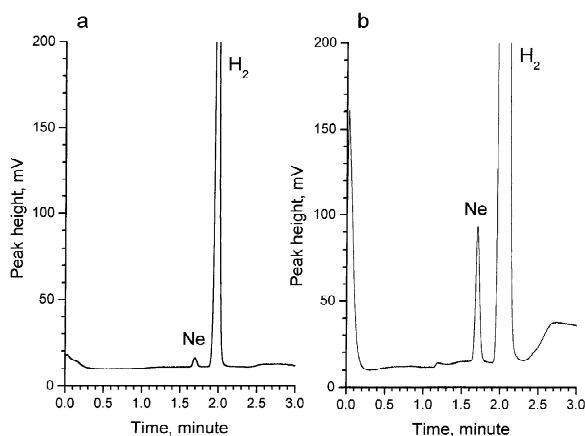


Fig. 4. Examples of neon analysis in water equilibrated with the atmosphere at 20 °C, (a) without sample enrichment, (b) with sample enrichment.

injected to the GC system, yielding the neon peak presented in Fig. 4a. Such a peak is too low to perform a quantitative analysis of neon concentration in water; therefore, sample enrichment is needed.

The enrichment system consists of a trap filled with activated carbon immersed in liquid nitrogen and connected to the sample loop of the V10 valve (see Fig. 1). In 5 min after the introduction of sample from the head-space volume, oxygen and nitrogen are completely adsorbed in the trap, and neon fills in the sample loop (V). By switching the valve V10, neon present in the loop is injected to the GC. An example of the neon peak obtained from the head-space phase of 100 cm<sup>3</sup> is shown in Fig. 4b for water in equilibrium with the atmosphere at 20 °C.

### 3. Discussion and conclusions

Measurements of neon concentrations with a good detection level are shown to be possible with PDHID, which is an additional advantage of that universal detector. However, the generation mechanism of the neon signal remains unclear. In another non-commercial pulse discharge detector used earlier [7], the sample was passed through the discharge zone, where neon was directly ionised. It is interesting that for such detectors doping with neon results in an increase of the neon signal, and a slight decrease of signals for other stable gases [6].

Following the manufacturer's advice, the best stability was obtained for the helium flow-rate through the column at least four times lower than the flow-rate through the discharge zone, though the measuring system stabilises in a few hours. However, each interruption of the chromatograph work results in a different current level displayed on the control unit, which means a slight change in detector sensitivity. Therefore, frequent calibration is necessary; in the present work atmospheric neon was used for calibration.

In the present work a PD-D2-I detector was used in which the sample does not pass the discharge zone. In the opinion of Wentworth et al. [8], the detection level in such a detector is 5 to 10 times worse for stable gases than for a detector in which sample passes through the discharge zone. However, within the present work, the detection level in the PD-D2-I detector for neon is shown to be the same as that obtained for the neon-doped Hitachi HDPID system [6]. It is also shown that for the PD-D2-I detector, doping leads to a linear characteristic without an improvement of the detection level. The signal is generated at some distance from the discharge zone from which excited helium dimers emit radiation in the energy range of 17.86–19.7 eV [7], 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 neon ionisation occurs. Perhaps in the PD-D2-I detector with neon doping, similar processes occur to those in the PD-D2 detector doped with Ar, Kr and Xe [13,14].

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### References

- [1] E. Mazor, *Geochim. Cosmochim. Acta* 36 (1972) 1321.
- [2] G.B. Wilson, G.W. McNeill, *Appl. Geochem.* 12 (1997) 747.
- [3] T.H.E. Heaton, J.C. Vogel, *J. Hydrol.* 50 (1981) 201.

- [4] L.N. Plumer, E. Busenberg, S. Drenkard, P. Schlosser, B. Ekwurzel, R. Weppernig, J.B. McConnell, R.L. Michel, *Appl. Geochem.* 13 (1998) 1017.
- [5] R. Sugisaki, K. Taki, *Geochem. J.* 21 (1987) 21.
- [6] H. Ogino, Y. Aomura, *J. Chromatogr. A* 659 (1994) 381.
- [7] W.E. Wentworth, S.V. Vasin, S.D. Stearns, C.J. Meyer, *Chromatographia* 34 (1992) 219.
- [8] W.E. Wentworth, H. Cai, S. Stearns, *J. Chromatogr. A* 668 (1994) 135.
- [9] E. Broś, J. Lasa, *J. Chromatogr.* 174 (1979) 273.
- [10] E. Broś, J. Lasa, *Chromatographia* 13 (1980) 567.
- [11] F. Poy, R. Verga, Characteristics and performance of a new helium ionization detector GC system, in: Presented at USSR–Italy Symposium, Tbilisi, 27–29 October, 1970.
- [12] I. Śliwka, J. Lasa, *Anal. Chem. (Warsow)* 45 (2000) 59.
- [13] G. Gremand, W.E. Wenworth, A. Zlatkis, R. Swatloski, E.C.M. Chen, S.D. Stearns, *J. Chromatogr. A* 724 (1996) 235.
- [14] W.E. Wenworth, N. Helias, A. Zlatkis, E.C.M. Chen, S.D. Stearns, *J. Chromatogr. A* 795 (1998) 319.