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Selective enhancement for neon detection in a helium discharge photoionization detector

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ABSTRACT

The helium discharge photoionization detector (HD-PID) is a very reliable and highly sensitive gas chromatographic detector for the determination of trace amounts of inorganic gases. However, the sensitivity of the HD-PID is poor for neon, similarly to a helium ionization detector (HID). The improvement of the HD-PID sensitivity, especially for neon, was studied. When helium containing 3.8 ppm (v/v) of neon was used as the helium discharge gas, the results obtained showed that the sensitivity for neon could be improved sixfold compared with that of the HD-PID under ordinary operating conditions.

INTRODUCTION

In the trace determination of inorganic compounds by gas chromatography, highly sensitive and universal detectors, such as the helium ionization detector (HID) [1] and the helium discharge photoionization detector (HD-PID) [2], have been widely used [3–9]. The HID seems to be currently the most sensitive detector for inorganic compounds such as noble gases (except neon), oxygen, nitrogen and carbon monoxide. However, the characteristics of the HID response are extremely affected by the purity of the helium carrier gas, its flow-rate, the applied potential, helium pressure, the temperature of the detector, etc.

Many efforts have been made to evaluate and improve the characteristics of the detector response, such as sensitivity, polarity and dynamic linear range, during the past decade. For example, the effects of helium purity and of adding hydrogen to the helium carrier gas were examined in order to evaluate the HID responses such as sensitivity and the polarity of response for helium, neon, argon, nitrogen, oxygen, methane and carbon monoxide [10–14]. Other experiments provided optimum conditions for operating the HID at maximum sensitivity and indicated that if the detector was designed with a very small volume, the response of the HID would be high and positive to all gases [15]. Further, some experiments were carried out in order to evaluate the effects of adding gaseous additives to the helium carrier gas. The results showed that if the applied voltage of the HID is more than 350 V, the addition of hydrogen, argon, oxygen or nitrogen gives an increase in the HID response, whereas if the applied voltage is less than 350 V, the HID response decreases [10]. However, it is essential that the HID is operated with caution because of the β-rays from tritium. On the other hand, the HD-PID does not use a radioactive material and has a similar sensitivity to that of the HID.

In the past few years, we have successfully developed techniques for the determination of trace impurities such as inorganic gaseous compounds in oxygen [6], hydrogen [7] and nitrogen [8] by means of a gas chromatograph combined with an HD-PID and precolumns packed with

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Cu–Zn catalyst for oxygen, $LaNi_5$ hydrogen storage alloy for hydrogen and Ti–Mn hydrogen storage alloy for nitrogen; these precolumns were used to remove the main gas (base gas) completely from a sample. However, the sensitivity of the HD-PID for neon was still poor and similar as that of the HID and the determination of trace levels of neon remained a difficult problem in gas analysis.

The HD-PID is based on the following principles: (1) a discharge in helium under atmospheric pressure emits radiation with a wavelength in the range *ca.* 600–1100 Å [2]; and (2) the photons emitted are used to ionize most kinds of compounds that have a lower ionization potential than that of helium.

A glow discharge is maintained by the emission of electrons from the cathode by a number of processes such as positive ion bombardment, photoelectric emission and collisions with excited atoms [1]. The ionization mechanism is considered to be based on the Penning effect, but has not yet been fully explored. On the other hand, the ionization potential of neon is 21.56 eV, which is close to that of helium (25.58 eV) and higher than that of metastable helium (He*, 19.8 eV), so that the response for neon is extremely poor compared with those of other gases, which have lower ionization potentials than helium. Therefore, if the HD-PID is used for inorganic gas analysis under ordinary operating conditions, the relative sensitivity for neon is less than 1% of that for other gases such as argon, nitrogen, oxygen and methane; the sensitivity of the HD-PID for neon was similar to that of a thermal conductivity detector.

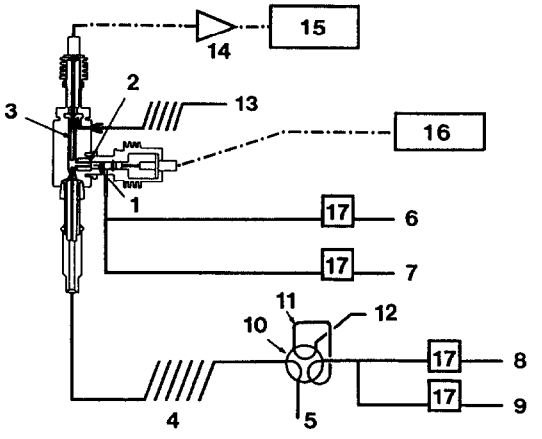

Fig. 1. Flow diagram of experimental apparatus. 1, 2 = Glow discharge electrodes; 3 = ion collector electrode; 4 = analytical column; 5 = helium carrier gas; 6 = neon source gas; 7 = helium discharge gas; 8 = standard gas; 9 = helium as diluting gas; 10 = six-port rotary valve with air actuator; 11 = 1.23-ml sample loop; 12, 13 = gas outlets; 14 = amplifier; 15 = computerized integrator; 16 = high-voltage power supply; 17 = mass flow controller.

In recent years, we have investigated the application of the GC–HD-PID system to the determination of trace gases in pure gases such as hydrogen, nitrogen and oxygen. In the course of these studies, it was found that the neon sensitivity could be improved by adding a trace amount of neon to the helium discharge gas. This paper describes the selective enhancement of neon detection in the HD-PID.

EXPERIMENTAL

A gas chromatograph equipped with an HD-PID (GC-263-30; Hitachi, Tokyo, Japan) was used. A flow diagram is shown in Fig. 1. Helium (99.99999%; Toyo Sanso, Kanagawa, Japan) was used as the carrier and discharge gas. Two gas purifiers (Model PH; Valco, Houston, TX, USA) were installed in the carrier gas and the discharge gas lines in order to prevent air contamination of the helium and gas mixtures as shown in Fig. 1. The following standard gases (Toyo Sanso) were used to evaluate the detector response under different conditions: (1) 1.02% and 107 ppm (v/v) neon in helium; (2) 1020 ppm (v/v) neon, 960 ppm (v/v) argon, 990 ppm (v/v) krypton and 1050 ppm (v/v) xenon in helium; and (3) 9.9 ppm (v/v) methane, 10.2 ppm (v/v) carbon monoxide and 9.7 ppm (v/v) oxygen in helium. The helium used in this experiment was previously confirmed to be free of neon by GC–MS (QP-300; Shimadzu, Kyoto, Japan). Mass flow controllers (Model 400; STEC, Kyoto, Japan) were used to prepare the desired concentration of neon in helium, which was fed as the discharge gas containing several to several hundred ppm of neon in helium. The concentrations of the prepared gas mixtures were calculated from the ratios of the flow-rates provided by the

mass flow controllers. In a similar manner, gas mixtures with various concentrations of neon, argon, nitrogen, etc., were prepared from standard gases.

RESULTS AND DISCUSSION

Effects of neon added to discharge gas

The effects of adding neon to the discharge gas were investigated with the use of helium containing neon at concentrations in the range 0–420 ppm (v/v). In order to evaluate the effect of neon addition, a gas mixture containing 7.5 ppm (v/v) neon, 6.2 ppm (v/v) krypton and 2.1 ppm (v/v) xenon in helium was prepared by diluting the standard gas with pure helium and was used as the sample gas. As shown in Fig. 2, the detector response to neon in the sample gas increased with increase in neon concentration in the discharge gas, then decreased rapidly after reaching a maximum response at around 3.6 ppm (v/v) neon and finally remained almost constant over the experimental range. However, the response for other gases such as krypton and xenon did not show this effect. This indicates that the addition of neon to the discharge gas selectively enhanced the response for neon in the sample gas.

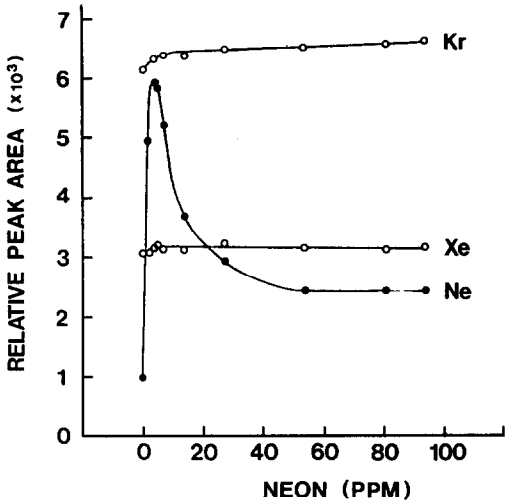

Fig. 2. Effect of neon concentration in helium as discharge gas on detector response. Sample gas contained 18.7 ppm (v/v) neon, 5.3 ppm (v/v) krypton and 5.7 ppm (v/v) xenon in helium. For other conditions, see text.

Analytical characteristics of enhanced HD-PID

To evaluate the characteristics of the enhanced HD-PID, a series of experiments were conducted with the following optimum GC conditions: analytical column, 3 m × 3 mm I.D. stainless-steel tube packed with molecular sieve 5A (177–250 μm); carrier gas, helium at 50 ml/min; oven temperature, 70°C; detector temperature, 100°C; discharge potential, 750 V; discharge gas, helium containing 3.6 ppm of neon at 40 ml/min; and sample loop, 1.23 ml. Using these HD-PID operating conditions, calibration graphs in order to confirm the linearity of response were determined for neon, argon, krypton and xenon over the wide range of 0–1000 ppm (v/v). The calibration graphs deviated from a straight line at concentrations above *ca.* 600 ppm (v/v) for argon, krypton and xenon, as shown in Fig. 3. The linearity profiles for these gases were similar to that obtained using pure helium as the discharge gas [6–9]. For neon, however, the detector response deviated significantly from a straight line, *i.e.*, the response is not proportional to the concentration of neon in the samples; if it had been then the dashed line in Fig. 3 would have

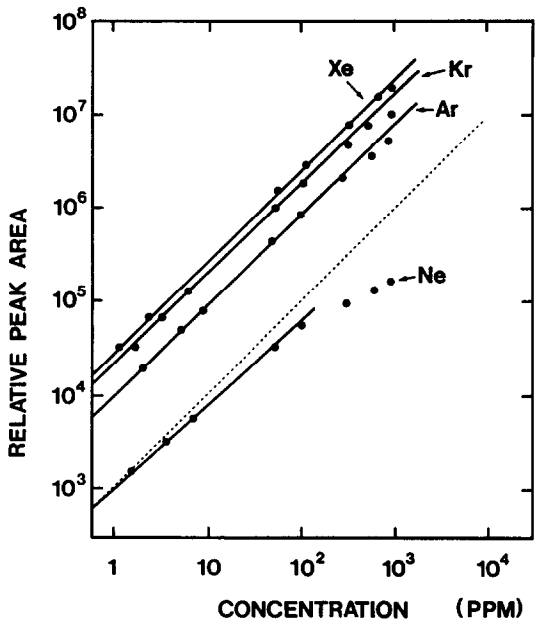

Fig. 3. Log–log calibrations for methane, neon, argon, nitrogen, carbon monoxide, oxygen, krypton and xenon. For GC conditions, see text.

been followed. The photoionization process with neon seems to be different to those with the other gases, as described below.

Consideration of neon enhancement

From the relationship between the detector response and the concentration of neon in the sample gas, it might be suggested that the enhancement for neon might not be due to the increase in the total intensity of photons emitted from both He* and Ne* as the effect of neon addition could not be clearly observed for krypton and xenon. Also, only photons emitted from Ne*, which has a potential energy corresponding to the excitation of neon, could be efficiently produced. The excited neon molecules emit electrons via reaction 2.3. The electrons can be detected as the signal of the detector. The mechanism of this enhancement is still unknown. As one possibility, the neon enhancement may be considered to be due to the following processes:

(1) He–Ne mixture discharge process:

$$He \longrightarrow He^*, Ne \longrightarrow Ne^* \quad (1.1)$$

$$He^* + Ne \longrightarrow Ne^* \quad (1.2)$$

$$Ne^* \longrightarrow Ne + h\nu_{neon} \quad (1.3)$$

(2) photoionization process for neon in a sample:

$$Ne_{sample} + h\nu_{helium} \longrightarrow Ne^*_{sample} \quad (2.1)$$

$$Ne_{sample} + h\nu_{neon} \longrightarrow Ne^*_{sample} \quad (2.2)$$

$$Ne^*_{sample} \longrightarrow Ne^+_{sample} + e^- \quad (2.3)$$

Hence the response of the detector for neon is expected to be the sum of the response obtained from the excited neon (Ne^*_{sample}) produced through reactions 2.1 and 2.2. This means that the intensity of emission, which can be absorbed by neon molecules in sample gases, may be increased more selectively and intensively than that of the emission obtained from only a helium discharge. However, it is not clear why only the neon response could be enhanced by the addition of neon into the discharge gas.

Analytical performance of enhanced HP-PID

The calibration graphs for neon, argon, oxygen, nitrogen, krypton, carbon monoxide, methane and xenon showed perfect linearity at concentrations below 10 ppm (v/v), as shown in Fig. 4: the calibration curve for neon was ap-

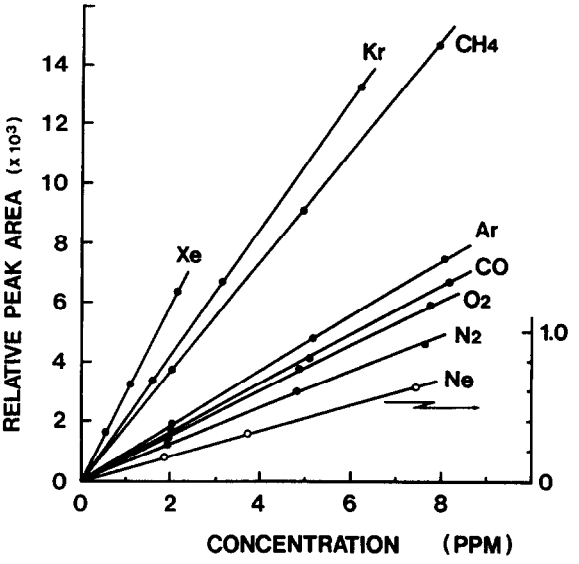

Fig. 4. Calibrations for neon, argon, nitrogen, carbon monoxide, oxygen, krypton and xenon in the range 0–10 ppm (v/v). The scale of peak area for neon is expanded five times relative to the others. For GC conditions, see text.

TABLE I

COMPARISON OF ANALYTICAL DATA OBTAINED WITH THE IMPROVED HD-PID AND ORDINARY HD-PID

Detector	Peak area corresponding to 2 ppm (v/v) of each component (arbitrary units)							
	Ne	O_2	Ar	N_2	Kr	CH_4	CO	Xe
Enhanced HD-PID (*A*)	1758	14 924	19 283	13 197	42 759	37 612	16 729	60 838
Ordinary HD-PID (*B*)	293	18 511	22 677	16 515	48 845	45 531	21 039	69 874
Ratio *A*/*B*	6.0	0.81	0.85	0.80	0.88	0.83	0.80	0.87

TABLE II

REPRODUCIBILITY OF THE DETERMINATION OF ppm LEVELS OF NEON, OXYGEN, ARGON, NITROGEN, KRYPTON, METHANE, CARBON MONOXIDE AND XENON IN HELIUM

Run No.	Peak area of components detected (arbitrary units)							
	Ne (1.87 ppm, v/v)	O_2 (1.94 ppm, v/v)	Ar (2.02 ppm, v/v)	N_2 (1.92 ppm, v/v)	Kr (1.56 ppm, v/v)	CH_4 (1.98 ppm, v/v)	CO (2.04 ppm, v/v)	Xe (0.53 ppm, v/v)
1	1564	14 784	19 436	12 931	33 428	37 137	16 991	15 724
2	1712	14 645	19 586	12 792	33 435	36 835	17 195	16 921
3	1720	14 278	19 325	12 789	33 220	37 133	17 285	16 267
4	1684	14 254	19 419	12 481	33 313	37 278	17 367	16 800
5	1588	14 461	19 709	12 725	33 507	36 744	16 969	15 373
6	1583	14 361	19 423	12 689	33 143	37 228	16 764	15 832
7	1590	14 761	19 423	12 558	33 446	37 732	17 104	16 712
8	1673	14 580	19 510	12 527	33 376	37 134	16 832	15 082
9	1684	14 343	19 583	12 721	33 302	37 791	16 772	16 383
Average	1644	14 496	19 490	12 690	33 352	37 223	17 031	16 122
S.D.	58.3	191.9	110.7	136.7	111.2	331.4	209.0	616.5
R.S.D. (%)	3.55	1.32	0.57	1.08	0.33	0.89	1.23	3.82
Detection limit ($S/N = 3$)	0.22	0.07	0.02	0.05	0.02	0.02	0.09	0.13

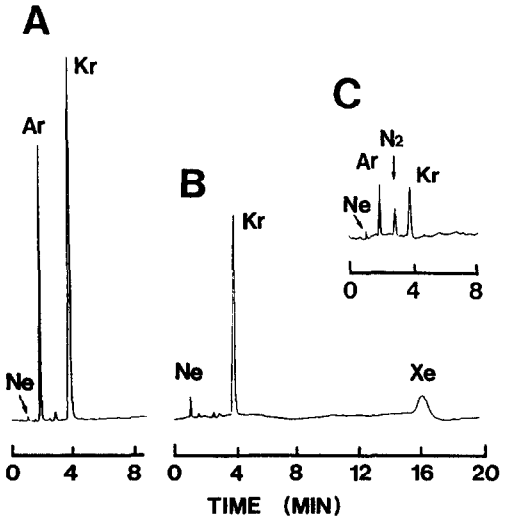

Fig. 5. Typical gas chromatograms. Sample gas: (A) 2.7 ppm (v/v) neon, 2.4 ppm (v/v) argon and 2.7 ppm (v/v) krypton in helium; (B) 1.9 ppm (v/v) neon, 1.5 ppm (v/v) krypton and 0.5 ppm (v/v) xenon in helium; (C) 0.2 ppm (v/v) neon, 0.4 ppm (v/v) argon, 0.2 ppm (v/v) nitrogen and 0.2 ppm (v/v) krypton in helium. For GC conditions, see text.

proximately linear at concentrations below 10 ppm (v/v). The sensitivities for several inorganic gases obtained with the present method were compared with those given by the ordinary method (without neon addition) and are summarized in Table I. The results show that only the neon sensitivity could be enhanced by the addition of neon to the discharge gas and that the sensitivity for the other gases decreased slightly, but there was not much difference between the results with the present and ordinary operating conditions [6–9].

The improved HD-PID could have sufficient sensitivity to be used as a detector for trace amounts of inorganic gas impurities including neon by the use of the present operating conditions. Typical gas chromatograms of standard gas mixtures obtained by (A) the ordinary method and (B and C) the present method are shown in Fig. 5. The minimum concentration of neon that could be detected with the ordinary operating conditions was a few ppm (v/v). By adding neon to the helium discharge gas, however, trace levels of neon in the sample gas could be detected. Analytical data such as the reproducibility and detection limits obtained with the present operating conditions are given in Tables II and III.

CONCLUSIONS

The improved HD-PID, which used a neon–helium mixture as the discharge gas, has a neon sensitivity *ca.* six times higher than that obtained by using pure helium as the discharge gas. It was confirmed that the improved HD-PID could be successfully and easily applied with an ordinary

TABLE III

REPRODUCIBILITY OF THE DETERMINATION OF TRACE LEVELS OF NEON, ARGON, KRYPTON, AND XENON IN HELIUM

Run No.	Peak area of components detected (arbitrary units)			
	Ne (0.2 ppm, v/v)	Ar (0.4 ppm, v/v)	Kr (0.2 ppm, v/v)	Xe (0.2 ppm, v/v)
1	178	4148	4951	7635
2	214	4346	5186	6898
3	180	4061	5407	7766
4	176	3831	4940	6997
5	170	3798	5102	7345
6	166	3644	4917	5825
7	190	3424	5070	6514
Average	182	3893	5082	6997
S.D.	14.9	291.1	161.0	625
R.S.D. (%)	8.16	7.48	3.17	8.94

gas chromatograph and that the determination of neon at sub-ppm (v/v) levels is possible. Further investigations will be made to understand this phenomenon of neon enhancement.

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