

## Helium direct current discharge ionization detector for gas chromatography

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### Abstract

A novel helium direct current discharge ionization detector for gas chromatography (GC) has been developed. Two platinum electrodes are applied to sustain the discharge. Helium was used as both the GC carrier and the discharge support gas. The effects of configuration and operational conditions on the response characteristics of the detector were studied. The analytical performance of the detector for the determination of some permanent gases such as H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, Ar, CO, CO<sub>2</sub> and CH<sub>4</sub> was proved to be ideal. The detector has the advantages of high sensitivity, good stability, little dependence on the purity of helium, and extremely simple configuration and structure. The analytical figures of merit were shown to be comparable with those of the conventional helium ionization detector and the discharge ionization detectors. Also, the ionization mechanism of the detector was investigated. Furthermore, some practical sample analyses were done and the results were satisfactory.

*Keywords:* Detection, GC; Helium d.c. discharge ionization detection; Ionization detection; Gases

### 1. Introduction

Ionization detection (ID) is a very important kind of chromatographic detection, especially for gas chromatography (GC). The most significant advantages of ID are its high sensitivity to species tested and simplicity in structure and configuration. Conventional ID methods include mainly flame ionization detection (FID), electron-capture detection (ECD), thermal ionization detection (TID) and photoionization detection (PID), etc. So far, FID [1,2] is still the most popular method in GC because

of its high sensitivity, wide linear dynamic range to hydrocarbons. However, for permanent gases and volatile inorganic compounds, sometimes important target species, FID cannot respond well and, furthermore, the operators have to risk the use of perilous gases to sustain the flame. ECD [3,4] is also a kind of highly sensitive ID, but only with good response to those species containing elements with higher electronegativities, such as halogens, oxygen and nitrogen. Generally, radioactive and hence harmful <sup>63</sup>Ni was used in ECD and, in this case, very little sample introduction was desired as its detection chamber can be easily contaminated. TID was also called nitrogen–phosphorus detection (NPD) [5,6]. Apparently, it can only respond well to species containing N and P atoms. PID [7,8] has been

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praised for having such advantages as higher sensitivity, better selectivity, easier operation and a wider linear dynamic range than FID. However, its application was still limited by following factors: (1) its UV light source can deteriorate after working for a while and as a result, the baseline of the detector drifts; (2) a severe problem, namely window pollution, cannot be easily overcome and, more significantly, the window materials are not transparent to the resonant lines of helium, resulting in PID being almost useless for inorganic gases; (3) fairly large dead volume and short life-time of the filament.

Argon ionization detection (AID) [9–12] and helium ionization detection (HID) [13,14] are two kinds of ID based on the Penning effect [15–17]. In 1955, Jesse and Sadauskis [18] found that an increase in the ion current could be observed when a trace amount of foreign gas was introduced into a rare gas under constant irradiation conditions. Based on this observation, Lovelock [9] developed a GC–AID method with a radioactive source. Berry [13] was the first to use this detection method with helium as the carrier gas. These two kinds of ID efficiently overcome lots of shortcomings of the traditional ID methods. Among their advantages, the most attractive one is their good universality. So, in the determination of inorganic gases, they showed very distinctive dominance. Since the ionization potential of helium (24.6 eV) is much higher than that of argon (15.8 eV), it is considerably more sensitive to organic compounds [19] than AID and other traditional ID methods and, besides, it is more suitable for the detection of inorganic species [13,14,20]. In this sense, HID is really “universal” because the ionization potential of helium is higher than that of almost all GC species and thus it is capable of ionizing all other compounds and almost all simple substances.

However, like ECD, most of the traditional HID systems [13,15–17,21–25] adopted perilous radioactive sources. There is no doubt that this caused a lot of problems, such as a lack of operation safety, sample contamination by the radioactive source and low tolerance of the radioactive source to high temperatures in practical analysis. In recent years, direct current discharge ionization detection (DCDID) [11,14,20,27–31] and pulsed discharge

helium detection (PDHID) [26,32–34] have attracted more and more attention due to their advantages such as simplicity in configuration, convenience in operation, high sensitivity, good versatility, and so on. The detectors developed by Kawazoe et al. [14] and by Wentworth et al. [26,32,33] and Madabushi et al. [34] are two typical types of DID systems for GC. Kawazoe et al. [14] used a platinum needle and a platinum ring as the d.c. discharge electrodes and the detection chamber and discharge chamber were vertical to each other. Wentworth et al. [26,32,33] and Madabushi et al. [34] adopted a pulsed high voltage to sustain the discharge between two opposite stainless-steel electrodes with platinum tips at the ends as the ionization source, and employed three polarization electrodes for applying a negative potential to repel generated electrons towards the collection electrode. It goes without saying that DID should also be regarded as another type of powerful HID when helium is used as the plasma working gas [14,20,26,27,29–34].

On the basis of the successful designs and detailed studies on different kinds of ID [12,28], a novel helium DCDID (HDCDID) was developed for GC detection of inorganic gases in our laboratory. In a cone-shaped chamber with a tangential gas inlet, the d.c. discharge was obtained between two parallel platinum plates with sanded zones on their opposite inner surfaces at the ends and with the detection chamber being co-axial with the discharge chamber. Part of the preliminary work on this detector has been published in the special editorial for the Second Changchun International Symposium on Analytical Chemistry [35]. In this paper, detailed, comprehensive and comparative studies on the dependence of the analytical performance of the detector on its configuration and structure, and the operational conditions such as the d.c. voltage, the flow-rates of the support gas ( $F_s$ ) and of the carrier gas ( $F_c$ ), and the purity of helium are reported. In addition, the ionization mechanism of the detector was investigated. Also, the detector was applied successfully to practical sample analyses. It was proved that the novel HDCDID, with an extremely simple configuration and structure, was highly sensitive to inorganic gases without severe dependence on the purity of both the support gas and the carrier gas.

## 2. Experimental

### 2.1. Apparatus, instrumentation, operational parameters and reagents

The block diagram of the apparatus is shown in Fig. 1. The main instrumentation components include a Model 102G chromatograph (with TCD and HID; Shanghai, Analytical Instruments Factory), a Model DWZ-301 voltage stabilizer (Beijing No. 6 Experimental Factory), a Model FH426B d.c. source (Beijing Comprehensive Instruments Factory), a Model XWT-164 recorder (Shanghai Dahua Instruments Factory) and three types of HDCDID systems (laboratory-built).

The general operational GC parameters are as follows: column, 3.5 m×3 mm stainless steel tube packed with 5A molecular sieve (180–210 μm) [for determination of CO<sub>2</sub>, a 2 m×3 mm stainless steel tube packed with GDX-101 (180–210 μm)]; column temperature, 50°C; volume of sampling loop, 200 μl; flow-rate of the carrier gas, 50–70 ml; polarization voltage, 250 V.

All the standard inorganic gases are of 99.999% purity. The purity of commercial helium (Beijing Analytical Instruments Factory) is 99.999% (as discharge support gas and GC carrier gas) and 99.99% (as one of the samples). Helium with a purity of better than 99.999% was obtained by purification of commercial helium (99.999% pure) with a liquid

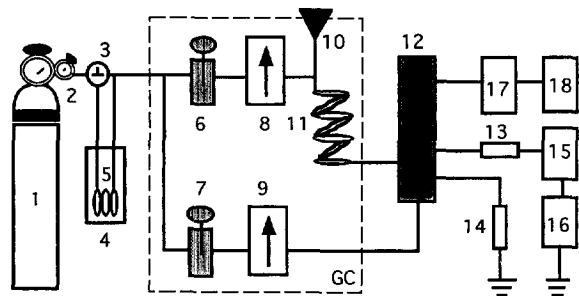


Fig. 1. Block diagram of GC-HDCDID system. 1=Helium cylinder; 2=pressure-reducing valve; 3=three-way valve; 4=liquid nitrogen trap; 5=purification column; 6,7=needle valve; 8,9=flowmeter; 10=sampling valve; 11=chromatographic column; 12=HDCDID; 13,14=current limiting resistance; 15=high-voltage supply; 16=d.c. voltage stabilizer; 17=multiplier; 18=recorder.

nitrogen-cooled stainless steel column (1 m×5 mm) packed with activated carbon and 5A molecular sieve. (This purification procedure was reported previously [14] and helium gas with a purity of 99.9999% could be obtained from commercial helium by using it). However, this purification procedure was required only when the effect of helium purity was being studied.

### 2.2. Configuration and structure of the HDCDID system

Fig. 2 presents the HDCDID systems in different configurations. On the whole, the HDCDID systems consist of a discharge chamber and a detection chamber. Two platinum electrodes are installed symmetrically in the discharge chamber to sustain the discharge of helium. In the detection chamber, a polarization electrode and a collection electrode [both 5.0 mm long, with an outer diameter of 4 mm and an inner diameter (I.D.) of 2.0 mm] are fixed co-axially, with a distance of 5.0 mm between them. The I.D. of the detection chamber is also 2.0 mm. The carrier gas and GC eluates are introduced at the mid-point between the collection chamber and the detection chamber, and are exhausted into air via a PTFE tube (1 m×1 mm I.D.), which is used to prevent air from back diffusing into the detection chamber. A 3 MΩ resistance is adopted as the d.c. current damper. The detectors are all made of stainless steel and PTFE is used as the insulating material. Depending on the shape of the discharge electrode and the configuration of the detection chamber, four types of HDCDID can be distinguished as follows:

#### 2.2.1. Detector A

As shown in Fig. 2a, a platinum needle (0.3 mm diameter) and a platinum ring (0.1 mm thickness and 1 mm I.D.) are employed as the discharge anode and cathode, respectively. The two discharge electrodes are vertical to each other. A point discharge can be observed between the point of the needle and the inner cycle of the ring when a suitable d.c. voltage is exerted on them. The discharge chamber is a cylinder (2 mm I.D.).

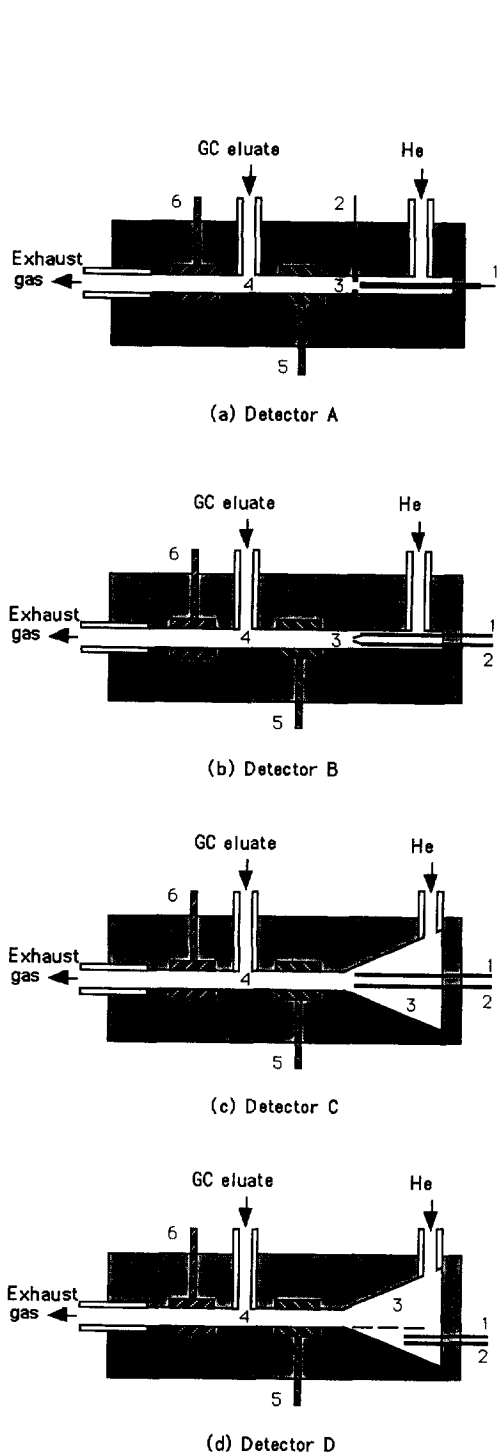


Fig. 2. Schematic presentation of HDCDID systems. 1=Discharge cathode; 2=discharge anode; 3=discharge chamber; 4=detection chamber; 5=polarization electrode; 6=collection electrode.

### 2.2.2. Detector B

Two platinum slivers (10 mm in length, 3 mm in width and 0.1 mm in thickness) placed in parallel with a 1.0-mm space between them are used as discharge electrodes. The end portion of the electrodes form an imperfect "V" with an end gap of 0.5 mm (Fig. 2b) and, in this way, a stable discharge can be restricted at the parallel edges of the V section of the electrodes. The configuration of the discharge chamber is the same as that in detector A.

### 2.2.3. Detector C

Two completely parallel platinum slivers are used as discharge electrodes, as presented in Fig. 2c. The distance between the two electrodes is 1.5 mm. It should be noted that 1.5 mm long areas on the opposite inner surfaces at the end of each electrode, were carefully sanded with abrasive paper, so that a luminous plasma column with bright and dark zones could be observed when a suitable d.c. voltage was applied across them. Another key point of the design is that the discharge chamber takes the form of a 5-ml cone-shaped chamber with a tangential gas inlet.

### 2.2.4. Detector D

The discharge electrodes and the discharge chamber are the same as those in detector C. As shown in Fig. 2d, the only difference is that the position of the discharge electrodes in detector D deviate to one side of the discharge chamber rather than being fixed co-axially, as in detector C.

## 3. Results and discussion

### 3.1. Optimization of HDCDID

#### 3.1.1. Optimization of operational conditions of the HDCDID systems

To evaluate the analytical characteristics of the HDCDIDs developed, the effects of working conditions such as the  $F_s$ , the  $F_c$ , the d.c. voltage across the discharge electrodes, as well as the purity of helium were investigated in detail.

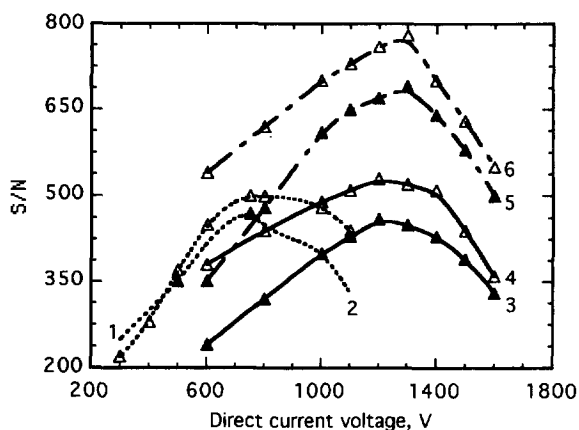


Fig. 3. Effect of discharge voltage on  $S/N$ . 1,2=detector A; 3,4=detector B; 5,6=detector C; 1,3,5= $O_2$ , 1.9 ppm; 2,4,6= $CO$ , 2.5 ppm. Flow-rate of the carrier gas, 60 ml/min; polarization voltage, 250 V; flow-rate of the support gas: 20, 90 and 95 ml/min for detectors A, B and C, respectively.

#### Direct current voltage

As illustrated in Fig. 3, an optimum range of d.c. voltage exists for each type of detector. The signal-to-noise ratios ( $S/N$ ) of the detectors for  $O_2$  and  $CO$  increase almost linearly with the d.c. voltage, when it is relatively low. When the d.c. voltage goes over the optimum value, the  $S/N$  falls sharply. The reason for this phenomenon is as follows: at a d.c. voltage below the optimum value, the discharge is in corona mode. In this case, the discharge is relatively stable and, hence, the noise produced on the collection electrode increases more slowly with the d.c. voltage compared with the signal. As a result, the  $S/N$  for each type of detector increases as the d.c. voltage rises. However, when the d.c. voltage goes over the optimum value, the corona discharge turns into arc discharge. In this case, the noise increases more rapidly than the signals with the rise in d.c. voltage and, as a consequence, the  $S/N$  decreases sharply. Another trend was also shown in Fig. 3, namely, point discharge can be obtained more easily than plate discharge. For detector A, even at a d.c. voltage below 300 V, the discharge can be formed and, at about 750 V, the  $S/N$  has reached its maximum. For detectors B and C, as far as the initial discharge voltage and the optimum voltage for  $S/N$  are concerned, they are superior to detector A. However, there is little difference between detector B and C in

this respect, because they both adopt a plate discharge.

#### Flow-rate of the support gas

Generally speaking, there is a synergistic effect between the optimum  $F_s$  and the optimum  $F_c$ . Therefore, it is necessary to optimize them by a multivariate method. However, it was found experimentally that the  $F_s$  had a greater effect on the response characteristics of the detector than the  $F_c$ , and the  $F_c$  only had a small effect in a fairly wide range. So, a univariate optimization procedure was still convenient and sufficient to reveal the trends of the effect of the operating parameters. Therefore, in order to study the effect of the  $F_s$ ,  $F_c$  was first set at a suitable value of 60 ml/min.

The role the support gas plays is to sustain the d.c. discharge and hence to provide the necessary active species for ionizing GC eluates. It was found experimentally that the  $F_s$  affected not only the stability of the plasma but also the sensitivity of the detector. A  $F_s$  that is too low produces too few active species, however, when it is too high it reduces the concentration of both the analyte and the active species, as well as the residence time of an analyte in the detection chamber. The noise under both circumstances is high due to the decreased stability of the discharge. Therefore, an optimum  $F_s$  value also exists for obtaining a maximum  $S/N$  for each species tested (Fig. 4). The  $S/N$  curves can be interpreted based on the two effects of the discharge gas. One is to increase the density of energetic particles (metastable particles, ions, electrons and photons), and the other is to reduce the concentration and the residence time of the analyte in the detection chamber [27]. The initial increase in the  $S/N$  at lower discharge support gas flow-rates is caused by the former effect. The latter effect, of course, reduces the ionization efficiency, and thus a sharp decline in the region of higher discharge support gas flow-rates is observed. In addition, Fig. 4 shows that the optimum  $F_s$  for detector A is far lower than that for detectors B and C. This is still a result of the different discharge modes because a point discharge can be formed at much lower  $F_s$ . This may be one of the basic reasons for some of the disadvantages associated with detector A.

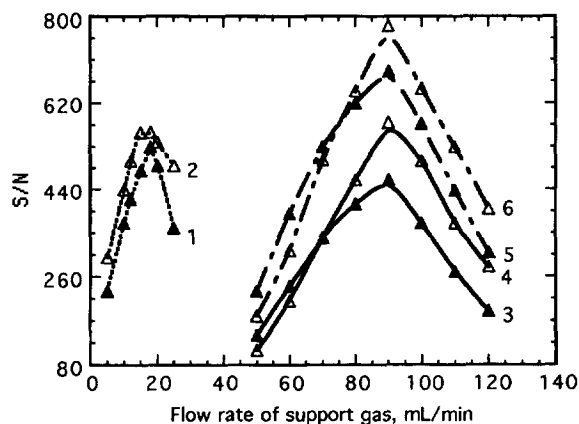


Fig. 4. Relationship between  $S/N$  and the flow-rate of the support gas. 1,2=detector A; 3,4=detector B; 5,6=detector C; 1,3,5= $O_2$ , 1.9 ppm; 2,4,6=CO, 2.5 ppm. Flow-rate of the carrier gas, 60 ml/min; polarization voltage, 250 V; discharge voltage: 750, 1200 and 1300 V for detectors A, B and C, respectively.

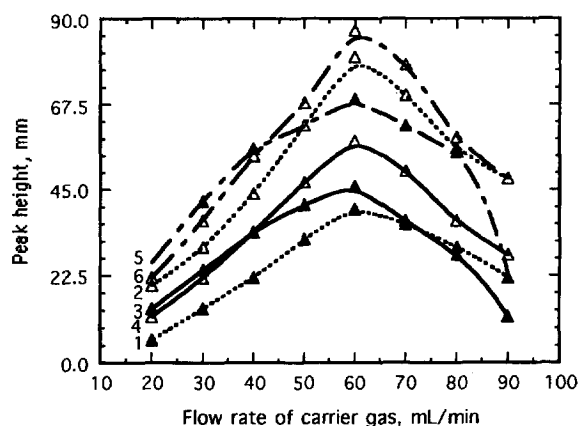


Fig. 5. Effect of the carrier gas flow-rate on the response. 1,2=detector A; 3,4=detector B; 5,6=detector C; 1,3,5= $O_2$ , 1.9 ppm; 2,4,6=CO, 2.5 ppm. Polarization voltage, 250 V; for detector A: d.c. voltage, 750 V;  $F_c$ , 20 ml/min; for detector B: d.c. voltage, 1200 V;  $F_c$ , 90 ml/min; for detector C: d.c. voltage, 1300 V;  $F_c$ , 95 ml/min.

#### Flow-rate of the carrier gas

The practical  $F_c$  is limited by the GC operating conditions and the structure of the detector. An  $F_c$  value that is too low is not beneficial for improving the chromatographic column efficiency and can cause peak broadening. In fact, it is impossible for the detector to be absolutely sealed against the atmosphere, so, a minimum  $F_c$  is also required to minimize atmospheric diffusion. For a 3-mm I.D. packed column, the optimum  $F_c$  for chromatographic separation would be approximately 40 ml/min. As illustrated in Fig. 5, the curves all present a maximum value at an  $F_c$  value of approximately 60 ml/min. So, the optimum  $F_c$  for detection is basically appropriate for separation in this GC–HDCDID system. Above the optimum value, any further increase of the  $F_c$  will decrease the response of the detector because a high  $F_c$  will reduce the ionization efficiency and shorten the residence time of analytes and hence reduce the signals. What should be pointed out is that an auxiliary gas should be added to the system after the column if HDCDID is coupled with a capillary column, as used in many capillary column GC systems.

It was generally believed that, for concentration-sensitive detection, the peak heights of analytes should be constant with variation of the  $F_c$ , while the peak areas should be inversely proportional to the  $F_c$ .

Also, for mass-sensitive detection, the peak heights should be proportional to the  $F_c$  and the peak areas should be constant, no matter how the  $F_c$  changes in a suitable range. However, for the detectors developed in this study, neither of these phenomena was observed. Therefore, HDCDID is neither purely mass-sensitive nor purely concentration-sensitive [36]. In other words, HDCDID has the response features of both mass-sensitive and concentration-sensitive detection [23,37].

To make more clear the significant dependence of the response characteristics of the HDCDID systems on their configuration and structure, a comparison of optimum operational conditions are summarized in Table 1. Obviously, the optimum conditions depend significantly on the discharge mode. In fact, the optimum conditions for detectors B and C (both with plate discharge) are relatively similar and are very different from those for detector A with a point discharge.

#### Polarization voltage

There are two competitive processes in the formation of the ion current related to the species of interest. One is the ionization of the species to produce cations and electrons, which is beneficial for the increase in ion current; the other is the recomb-

Table 1  
Optimum operational conditions for HDCDID systems

	Detector A	Detector B	Detector C
Discharge voltage (V)	650–800	1100–1300	1200–1400
Flow-rate of support gas (ml/min)	16–24	80–100	85–100
Flow-rate of carrier gas (ml/min)	55–70	50–70	50–75

nation of cations with electrons, which makes the ion current decrease. Generally speaking, the polarization voltage is used to provide an electrical field so that the movement of charged particles with opposite polarity can be directed and hence it reduces the opportunity for these charged particles to recombine before they are efficiently collected. So, the polarization voltage has a tangible influence on the basic current, noise and response signals. Taking detector C as an example, the dependence of the response of  $\text{CH}_4$  on the intensity of the electric field between the polarization electrode and the collection electrode has a shape similar to that typically obtained for the HID [10] and the DCDID [14], as shown in Fig. 6. A compromising value of polarization voltage, 250 V, was chosen in this study.

#### Purity of the support gas and the carrier gas

Early in the 1960s, Berry [13] and Bourke et al. [21] pointed out that one apparent disadvantage of a helium ionization detector was that considerable efforts must be made to ensure the purity of the

helium if optimum sensitive and “universal” detection was to be realized. The work by Goldbaum et al. [22] also indicated that it was only at extremely high helium flow-rates (ca. 300 ml/min) that the proper environment in the detector to ionize atmospheric gases could be obtained using commercial helium. However, the new detector developed in this study can function with helium as both the support and the carrier gas at a lower flow-rate (<100 ml/min) without the need to purify the gas. For such a purpose, it is surely important to keep the system sealed well to avoid the back diffusion of air at the outlet of the system. Fig. 7 shows the effect of the length of PTFE exhaust tube on the  $S/N$  ratios of CO and  $\text{N}_2$  for detector C. Obviously, for a 1-mm I.D. PTFE tube, a length of 30 cm is sufficient to prevent the back diffusion of air.

Table 2 lists the dependence of the analytical performance of detector C on the purity of helium. When helium with a higher purity than 99.999% (obtained by purifying the commercial helium with a purity of 99.999%, as previously stated in Section

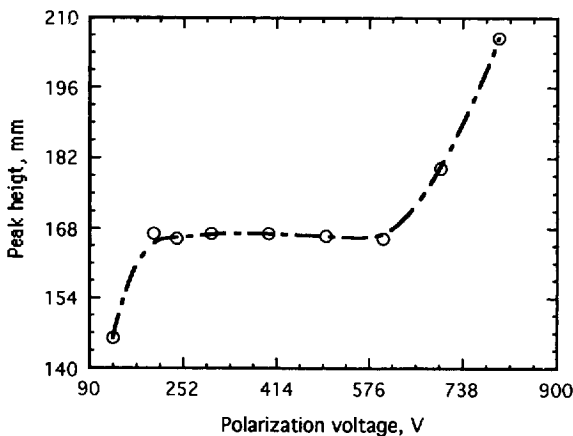


Fig. 6. Response of detector C to  $\text{CH}_4$  as a function of polarization voltage.  $\text{CH}_4$ , 3.2 ppm. Discharge voltage, 1300 V; flow-rate of the support gas, 95 ml/min; flow-rate of the carrier gas, 60 ml/min.

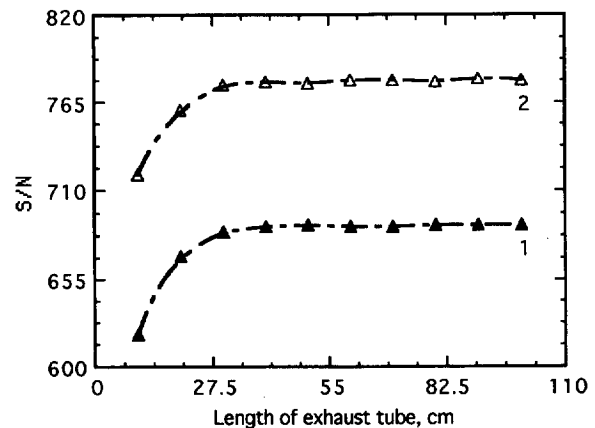


Fig. 7. Dependence of  $S/N$  on the length of the PTFE exhaust tube. 1=O<sub>2</sub>, 1.9 ppm; 2=CO, 2.5 ppm. Discharge voltage, 1300 V; flow-rate of the carrier gas, 95 ml/min; flow-rate of the support gas, 60 ml/min; polarization voltage, 250 V.

Table 2  
Effect of the purity of helium on the analytical performance of detector C

Purity (%)	Basic current (A)	Noise (A)	Detection limit (ppb, v/v)		
			Ar	CH <sub>4</sub>	N <sub>2</sub>
99.999	1.2·10 <sup>-9</sup>	1.8·10 <sup>-13</sup>	2.0	18	6.0
99.9999	1.5·10 <sup>-9</sup>	1.6·10 <sup>-13</sup>	1.8	12	5.2

2.1) was used instead of that with a purity of 99.999%, the noise of the detector did not vary. Very little variation occurred for the basic currents and the detection limits. It seems that the purity of helium had less influence on HDCDID than on conventional HID which uses radioactive material such as scandium tritide as the ionization source [23]. One reason why a significant difference between different grades of purity of helium was not observed may be that there were leaks that made the relatively pure helium become impure in the HDCDID system, because the use of PTFE itself may be a source of leakage, caused simply by diffusion through the material, though the back diffusion in the PTFE exhaust tube was efficiently overcome. However, the detector still responded well, even in this case. Therefore, for the HDCDID system, the configuration and the structure of the detector are considered to play more significant roles than the purity of the support and the carrier gas. Of course, this does not mean that it is unnecessary to guarantee that the helium is of very high purity in the detector; on the contrary, the purity of helium is still very important for detection of trace chromatographic species.

### 3.1.2. Performance comparison of the HDCDID systems

It was shown experimentally that the detection ability of the HDCDID depended significantly on the stability of the plasma. Obviously, the stability of the plasma was greatly affected by the shape of the discharge electrodes as well as by the configuration of the discharge chamber. Stabilization of the discharge and hence reduction of the noise of the detector was extremely important for improving the analytical performance of the detector.

For the purpose of evaluating the response characteristics and the analytical performance of the detec-

Table 3  
Comparison of the response characteristics of HDCDID systems

Detector	Response characteristics			
	BC (A)	N (A)	DL (ppb, v/v)	MOLR
A	4.0·10 <sup>-9</sup>	1.0·10 <sup>-12</sup>	13	4
B	1.5·10 <sup>-9</sup>	5.0·10 <sup>-13</sup>	32	4
C	1.2·10 <sup>-9</sup>	1.8·10 <sup>-13</sup>	4	4
D	1.0·10 <sup>-9</sup>	1.7·10 <sup>-13</sup>	4	4

BC=Basic current, N=noise, DL=detection limit, MOLR=magnitude orders of the linear range; O<sub>2</sub> was the species tested.

tors, the basic current, noise and detection limits for several permanent gases with each type of detector were investigated, and the results are shown in Tables 3 and 4. It can be seen clearly that, of the four types of HDCDID systems, the noise of detector A is apparently higher than that of the other types, because, in the case of detector A, the discharge drifts continuously along the ring during the discharge. Although the discharge can be easily sustained, the *S/N* is not as good as that. For detector A, the *S/N* ratio also depends greatly on the machining precision of the discharge electrodes and the chamber, as well as on the flow stability of the support gas. For detector C, the stability and sensitivity of detection were much improved and hence the *S/N* was significantly enhanced. There were two reasons for this: (1) a cone-shaped discharge chamber was employed to guarantee the stabilization of the support gas. As can be seen from Fig. 2c, the volume of the discharge chamber is far larger than that of the gas passage from the discharge chamber to the detection chamber, so, the unstable factors of

Table 4  
Comparison of the analytical performance of three types of HDCDID

Species	Detector A		Detector B		Detector C	
	DL	MOLR	DL	MOLR	DL	MOLR
Ar	6	5	4	5	2	5
CH <sub>4</sub>	2	5	45	5	18	5
CO	10	4	45	4	4	5
CO <sub>2</sub>	18	4	50	4	11	4
O <sub>2</sub>	13	4	32	4	4	4
H <sub>2</sub>	41	3	76	4	9	4
N <sub>2</sub>	79	3	57	3	6	4

DL=Detection limit, in ppb (v/v); MOLR=magnitude orders of the linear range.



fluid mechanics of the support gas can be efficiently buffered and, in addition, the tangential gas introduction mode was no doubt very beneficial for the reduction of the instability of the discharge; (2) the opposite surfaces of the end section of the discharge electrodes were carefully sanded with abrasive paper and, as a result, the discharge was fixed to this zone because the sanding procedure changed the homogeneity of the electronic field between the two electrodes and made it easier for this zone to break down the passing inert gas. As expected, no discharge drift like that in both detectors A and B was observed. The baseline drift of detector C was less than 0.02 mV/h and the R.S.D. for eleven replicate measurements of 1.9 ppm O<sub>2</sub> in standard samples was 2.8%. Moreover, the volume of the discharge was obviously larger than that of the former two types of detector and, therefore, this type of detector exhibited a higher sensitivity and better tolerance to the analytes, especially when compared with detector A. Table 5 shows that the analytical performance of detector C is also comparable with HID and similar DID.

### 3.2. Consideration of ionization processes

The knowledge of plasma species is very important in understanding the processes happening in analyte ionization. The plasma species of importance include those that are present in high number densities and those with relatively long lifetimes (>1 μs). In helium discharge, the energetic species include the ions (He<sup>+</sup>), the atomic triplet states (He<sup>m</sup>), the first molecular state (He<sub>2</sub><sup>m</sup>), the ground state of the molecular ion (He<sub>2</sub><sup>+</sup>), electrons (e) and photons (hν) [39]. The triplet states and the molecular ions are metastable species with relatively long

lifetimes, in the range of 1–10 μs at atmospheric pressure [40]. Among those energetic species, electrons (e), helium ions (He<sup>+</sup>) and metastable helium atoms (He<sup>m</sup>) are the three most important species as far as number density is concerned. These active species with rather high energies and photons were generally believed to be the energy carriers in the ionization process.

For DID, photoionization was always thought to be the main process in the ionization of analytes [14,27,41]. In order to find out to what extent the ionization of analytes depends on the photoionization in HDCDID, the position of the discharge electrodes in detector D was deviated to one side of the discharge chamber rather than fixed coaxially (as in detector C), so that the chromatographic eluates could not be directly irradiated by the ultraviolet photons from the discharge (Fig. 2d). Of course, other active species, as indicated above, could still reach the detection chamber to act on the eluates coming from the chromatographic column. It was found experimentally that the response characteristics with this configuration were very similar to those obtained with detector C, as listed in Table 3. Clearly, in detector C, the analytes were not mainly ionized by the direct irradiation of the ultraviolet photons emitted from the helium d.c. discharge. Moreover, as far as the relationship between the response and  $F_c$  is concerned, the fact is that HDCDID is neither purely mass-sensitive nor completely concentration-sensitive. We know that PID, in which the photoionization plays a key role in the ionization of tested species, is concentration-sensitive. Thus, the HDCDID system in this work should not be regarded as a pure PID system. By the way, if an optical window did exist between the detection chamber and the discharge chamber, it may be

Table 5  
Comparison of detection limits for permanent gases (ppb, v/v)

Species	HID [38]	GC-MS [38]	DID [38]	PDHID [26]	HDCDID <sup>b</sup>
H <sub>2</sub>	5	—	50	2.4	9
O <sub>2</sub>	50	1	10	2.8 <sup>a</sup>	4
N <sub>2</sub>	10	1	10	8.4	6
CO	25	10	5	3.2	4
CH <sub>4</sub>	5	10	5	0.8	18
CO <sub>2</sub>	5	0.1	15	—	11

<sup>a</sup> O<sub>2</sub> + Ar; <sup>b</sup> this work, detector C.

suitable to regard the HDCDID system as a PID system, as reported by Sevcik and Krysl [42], because, in this circumstances, only photons and not any other kinds of active species can reach the detection chamber. For HDCDID, besides the photons, all other sorts of active species could enter the detection chamber. Therefore, the ionization for HDCDID would be a mixture of various ionization processes. Since the micro-ionization procedures are extremely complex, further quantitative and theoretical description of the ionization processes cannot be presented. However, use of the detector will not be hindered by this.

### 3.3. Practical sample analysis

The concentration of CO<sub>2</sub> in air is becoming increasingly higher due to the wider use of fossil fuels. As a result, the global ecosystem has been threatened by the greenhouse effect. In agriculture, the growth of vegetables and other plants in a greenhouse is always strictly dependent on the concentration of CO<sub>2</sub>. Therefore, determination of the concentration of CO<sub>2</sub> quickly, accurately and conveniently is now a very important subject in geochemistry, environmental chemistry and agrochemistry.

The analysis of impurities at the sub-ppm level in high purity gases has attracted great attention in recent years, especially in the semiconductor, military, functional material and aeronautical industries. In order to ensure the quality of high-purity gas, the detection of impurities is necessary. For example N<sub>2</sub> and O<sub>2</sub> are two of the main impurities in inert gas in cylinders. The content of these is important in

determining the grade of the inert gas. Much of this analysis is done chromatographically. TCD and ultrasonic detection both fall into this category. However, their detection abilities are generally limited to the low ppm level.

To further evaluate the universality and practicability of HDCDID, CO<sub>2</sub> in air, and O<sub>2</sub> and N<sub>2</sub> in cylinder helium were determined with detector C. As expected, the results were quite comparable with those obtained with TCD and the commercialized HID, as illustrated in Table 6.

## 4. Conclusions

A new kind of HDCDID which responds sensitively and steadily to permanent gases such as H<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> and Ar has been developed. Compared with conventional HID, this HDCDID method is more convenient and safe to operate due to its use of a direct current discharge instead of radioactive materials as an ionization source and because there is less dependence on the purity of the support and carrier gas. The analytical performance of HDCDID is quite comparable with that of conventional HID (and the similar DID) method. Concerning the ionization mechanism, it was revealed that the chromatographic eluates were not mainly ionized by the ultraviolet emissions from the discharge. HDCDID has neither the response characteristics of a purely mass-sensitive detector nor that of a concentration-sensitive one. The detection method has been proved to be very powerful for measuring permanent gases in environmental samples and impurities in high purity gases. Since the configura-

Table 6  
Results of the measurement of CO<sub>2</sub> (ml/100 ml) in ambient gas samples and of N<sub>2</sub> and O<sub>2</sub> in cylinder helium (ppm, v/v)

Sample	Species determined	HDCDID (detector C)	TCD	HID	R.S.D. (%) <sup>b</sup>
<i>Environmental gas</i>					
Indoor air	CO <sub>2</sub>	0.048	0.051	—	2.6
Outdoor air	CO <sub>2</sub>	0.032	0.034	—	2.0
Flue gas	CO <sub>2</sub>	0.25	0.22	—	1.5
<i>Helium in cylinder<sup>a</sup></i>					
	O <sub>2</sub>	10.5	—	11.2	3.6
	N <sub>2</sub>	33.8	—	32.9	3.1

<sup>a</sup> Purity of helium, 99.99%; <sup>b</sup> for HDCDID.

tion and structure of the detector are extremely simple and the d.c. source can be made very compact (like that in a camera), it can be expected that this HDCDID system could be miniaturized and combined with a portable gas chromatograph for important on-site determination of permanent gases.

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