Shimadzu Review

Development of New Ionization Detector for Gas Chromatography by Applying Dielectric Barrier Discharge

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Abstract

A new gas chromatographic detector, dielectric barrier discharge ionization detector (BID), has been developed by applying atmospheric non-equilibrium plasma to a photo-ionization source. The relation between the type of dielectric barrier discharge and its stability, and the influence on the baseline stability by outgassing from the discharge cell were clarified. The electrometer of BID was optimally designed to reduce the baseline fluctuation even at high operating temperatures by improving electrical insulation of the electrometer. The detection limit of BID was less than 1.0 pgC/sec for n-dodecane, which is less than that of the flame ionization detector (FID), and the linearity was typically 10⁵. The relative sensitivities for chlorine-containing compounds and alcohols were more than 10 times that of FID. The SN ratio of the response for inorganic sample was 100 times greater than that of thermal conductivity detectors (TCD).

Keywords: Gas chromatography, Ionization detector, Dielectric barrier discharge

1. Introduction

The various types of detector conventionally used for chromatography include the thermal conductivity detector, electron capture detector, flame ionization detector, flame photometric detector, and flame thermionic detector. The flame ionization detector (FID) and thermal conductivity detector (TCD) are the most commonly used of these detectors. The FID uses a hydrogen gas flame to ionize the sample components in the sample gas and measure the resulting ion current. It achieves a wide, 7-digit dynamic range. The TCD measures changes in the thermal conductivity of the gas. As it is sensitive to samples other than the carrier gas, it is used for detection of inorganic gases which cannot be measured by an FID.

On the other hand, the discharge ionization detector (photoionization detector) has a long history since Lovelock proposed the discharge ionization detector in 1960¹. This detector ionizes the sample with vacuum ultraviolet light from a plasma created by an electrical discharge in rare gas and then measures the resulting ionization current. Applying a high voltage to opposing needle-shaped electrodes is the method generally used to create an electrical discharge in discharge ionization detectors².³

Although this method achieves an electrical discharge at relatively low voltages of several hundred volts, the high current flow causes burning of the electrodes and sputtering of the electrode material that result in changes or deterioration of the discharge characteristics. Therefore, enhancements to restrict overheating the electrodes have been proposed such as by using DC pulsed voltage source⁴.

The authors have developed a new dielectric barrier discharge ionization detector (BID) exploiting dielectric-barrier discharge in helium gas as an electrical discharge method that does not readily cause overheating and sputtering of the electrodes. This paper explains the BID detection principle and the construction of the detector. It then discusses the results of the optimization testing of the discharge conditions related to the detector performance and testing of modifications to the charge collector, and introduces some examples of actual measurements.

2. Ionization Principle

Dielectric-barrier discharge occurs when an alternating voltage is applied across the discharge electrodes when one or both of electrodes is coated with a dielectric material. The dielectric material inserted between the electrodes restricts the current flow, which suppresses overheating of the electrodes to maintain stable discharge. Selecting a chemically stable dielectric material should inhibit sputtering due to the plasma. Dielectric-barrier discharges are also known as silent discharges and have long been used for ozone generation. In 1988 Okazaki et al. performed dielectric-barrier discharges using helium as the discharge gas and alternating currents (several kV) at relatively low-frequencies (several kHz to several tens of kHz). This achieved stable, pulsed discharges at atmospheric pressure⁶. However, vacuum ultraviolet (13.5 to 17.5 eV) is created not only by dielectric-barrier discharge but is also emitted when excited helium molecules in the discharge in the helium gas return to their ground state. \( He_2 + \sum \rightarrow 2He + \sum \) This high-energy vacuum ultraviolet is able to ionize most samples analyzed by gas chromatography, with the exception of neon with very high ionization energies (21.6 eV).

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3. Detector Construction and Characteristics

3.1 Overall Construction

Fig. 1 shows a cross-sectional view of the developed BID. The arrows in the diagram show the directions of the gas flows (discharge gas and sample gas). The detector comprises a plasma generator and charge collector. The major component of the plasma generator is a quartz tube that passes through three cylindrical electrodes. High-purity helium gas is supplied through the discharge gas inlet tube at the top of the diagram. The two outermost of the three electrodes are grounded and an alternating high voltage (5 to 30 kHz, 5 to 10 kV) is applied to the central electrode. The walls of the quartz tube play the role of a dielectric barrier and dielectric-barrier discharge occurs inside the quartz tube between the two grounded electrodes. A bypass exhaust tube is connected between the plasma generator and charge collector to exhaust some of the discharge gas used for the plasma generation. (The role of bypass exhaust is described below.) The charge collector is located downstream of the discharge gas. It comprises two cylindrical electrodes separated by an insulator. A DC voltage is applied to the upstream electrode (bias electrode). The downstream electrode (collector electrode) is connected to a current amplifier. The generated ions collect on the collector electrode due to the electrical field between the bias electrode and collector electrode and are detected as a signal voltage by the current amplifier.

3.2 Dielectric-Barrier Discharge

A major feature of the BID is that the dielectric-barrier discharge inside the quartz tube generates a non-equilibrium plasma. The BID dielectric-barrier discharge generates a non-equilibrium plasma with an extremely low gas temperature. Measurements of the quartz tube surface temperature before and after plasma generation reveal no more than 5 °C temperature increase, making it difficult to accurately grasp the amount of heat. By removing the charge collector from the BID plasma generator and discharging the plasma gas to atmosphere, it is possible to generate a helium plasma jet, as reported by Engemann et al in 2005. Almost no sensation of heat is felt even if the plasma jet is played directly on to the skin (Fig. 2). The low heat generation reduces noise in the detector by restricting the causes of plasma fluctuations, such as temperature fluctuations in the plasma generator and outgassing from the plasma generator walls. The plasma generator construction in Fig. 1 clearly shows that the plasma impinges only on the wall of the quartz tube. Quartz has a high melting point and sputtering does not readily occur due to the plasma. Even if sputtering does occur, as the same material simply passes through the quartz tube inner wall, little change occurs in the condition of the inner wall. There is extremely low possibility of changes in the wall electrical resistance affecting the long-term stability of the plasma, as occurs with metal electrodes. Long-term operational testing of the detector revealed less than 15 % fluctuation in detector sensitivity (area value) and no significant change in the S/N ratio before and after a 3000-hour continuous discharge test.

3.3 Bypass Exhaust

One feature of the dielectric barrier discharge ionization detector (BID) is the bypass exhaust tube connected between the plasma generator and charge collector to exhaust some of the discharge gas. The role of the bypass exhaust is described below. It is not necessary to maintain a certain gas flowrate to cool the BID plasma generator, as described in the above Section 3.2. However, as outgassing from the tube inner wall occurs at a constant rate, problems with decreased gas purity can occur when the discharge gas flowrate is low. The discharge gas flowrate must therefore exceed a certain flowrate to achieve stable detector performance. Solvents or other high-concentration sample gases entering the detector can diffuse against the gas flow and cause contamination when they enter the plasma generator. A high flowrate in the plasma generator is desirable to avoid this problem. Conversely, a high discharge gas flowrate in the charge collector dilutes the sample gas and reduces the signal intensity. For this reason, a bypass exhaust is installed in the discharge ionization detector to allow a high flowrate to be maintained in the plasma generator while restricting the flowrate in the charge collector.

3.4 Verification of the Ionization Mechanism

As described in Section 2, the discharge ionization detector proposed by Lovelock et al ionizes the sample with vacuum ultraviolet light from a plasma created by an electrical discharge. On the other hand, the discharge ionization detector proposed by Monagle et al ionizes samples through Penning ionization due to metastable helium generated in the plasma. If Penning ionization were the dominant process for ion generation in the BID, more efficient ion generation could be achieved through the method of mixing all the discharge gas with the sample gas without the use of the bypass exhaust described above. The following comparison tests were performed to investigate the BID ionization process. Fig. 3 shows the two gas flow methods that were compared. In Fig. 3 (a), the BID bypass exhaust tube is sealed and the discharge gas is introduced from the top of the quartz tube. After flowing through the plasma generator it mixes with the sample gas in the charge collector. In Fig. 3 (b), the discharge gas enters through the bypass exhaust tube and flows in the opposite direction. The gas flow is split in an approximately 1:1 ratio between the plasma generator and charge collector. The gas flowing through the plasma generator exits from the uppermost tube (originally the gas inlet tube).
usual. Comparing the sensitivity (area values) for these two flows suggests that the sensitivity of the flow method in Fig. 3 (b) would be extremely low if Penning ionization due to metastable helium were the dominant process, as the metastable helium generated is evacuated from the top of the detector without mixing with the sample. However, if the vacuum ultraviolet light is dominant, there should be little difference between the sensitivity of the two flow methods.

Fig. 4 (a) shows the detector output signals when 6 ng methane gas sample was injected three times with a gas-tight syringe using the flow method in Fig. 3 (a). Fig. 4 (b) shows the detector output signals for the flow method in Fig. 3 (b). The tests were performed with 100 mL/min gas flowrate in both the plasma generator and charge collector. (However, the gas flow direction in the plasma generator is opposite in (a) and (b).) The mean peak area values were 2.3 nA•sec for (a) and 1.8 nA•sec for (b). Even flow method (b) with no mixed metastable helium achieves adequate ionization current, confirming the dominant role of vacuum ultraviolet light in ionization in the BID detector. Therefore, even losing some discharge gas in the bypass exhaust does not have a major effect on ionization efficiency. However, as the sample dilution rate is proportional to the gas flow rate in the charge collector, the gas flow in the charge collector is restricted and high ionization efficiency can be achieved.

The plasma contacting the metal electrode and of fluctuating plasma state due to thermionic emissions from the metal. To simplify observations of the discharge state, a plasma generator comprising a quartz tube connected to a branch tube and wound with copper tape (Fig. 5) was used to investigate the relationship between the discharge state and S/N ratio using a construction approximately equivalent to the BID. Both-side dielectric barrier discharge can be achieved by adjusting the applied voltage amplitude, as shown in Fig. 5 (a). The discharge conditions were 10 kHz power frequency, 5.8 kVp-p applied voltage amplitude, and 160 mL/min discharge gas flowrate. By increasing the applied voltage amplitude to 8.0 kVp-p, the discharge region expands and single-side dielectric barrier discharge occurs to the metal electrode inserted in the branch tube, as shown in Fig. 5 (b). The detector output for each discharge state was compared when a 6 ng methane gas sample was injected three times from a gas-tight syringe. (Fig. 6) Fig. 6 (a) shows the detector output with both-side dielectric barrier discharge (Fig. 5 (a)) and Fig. 6 (b) shows the output with single-side dielectric barrier discharge (Fig. 5 (b)). Single-side dielectric barrier discharge shows increased baseline noise and reduced S/N ratio compared to both-side dielectric barrier discharge.

4.2 Impurities from Plasma Generator Inner Walls

The purity of the discharge gas significantly affects the detector performance. Helium gas of 99.9999 % minimum purity is used to achieve high performance. This requires a gas supply via a helium purifier and materials other than stainless steel, such as plastic or copper, may not be used. Even if such measures are observed, the discharge gas contains outgas from the tube inner wall as impurities. As the BID dielectric barrier discharge ionization detector can ionize most substances except neon (Ne), the impurities in the discharge gas are also ionized and output as the baseline in the detector output signals. High levels of impurities increase the baseline output and cause detector output fluctuations due to the effects of ambient temperature and pressure. Therefore, reducing the impurity gas has the dual results of enhancing discharge stability and reducing the baseline output.

To investigate the pathways by which impurities enter the discharge gas, the impurities in the discharge were analyzed from the plasma emission spectrum. Fig. 7 shows the emission spectrum when a fused quartz tube (approx. 200 ppm OH content) was used in the plasma generator. In addition to the He (587.6, 706.5 nm) and HeI (640 nm) emission peaks, H (486.1, 656.3 nm) and O (532.9, 543.6 nm) emission peaks were also observed. However, the H and O emission peaks became significantly reduced (some of them lay below the observable limit) and the detector baseline output dropped from 5.9 nA to 3.4 nA when a synthetic quartz tube (5 ppm max. OH content) was used in the plasma generator. It confirms that selecting plasma generator materials with low levels of outgassing can reduce the baseline output.
5. Examples of Detector Outputs

The detector output was measured for several standard samples to compare the BID with the FID and TCD relating to response characteristics.

4.3 High-Temperature Characteristics of the Charge Collector

The ionization detector output current baseline is in the order of several pA to several nA. Therefore the leak current between the current collector bias electrode and collector electrode must also be in the order of several pA. As the electrical resistance of the insulators drops at high temperatures, increasing the leak current at high temperatures has a significant effect on the detector performance. Thus, detectors were made using two types of alumina insulators with different resistance properties (material a: 99% purity; material b: 99.5% purity). The 99.5% purity material b offers high volume resistivity at high temperatures. At 300 °C and above, the volume resistivity is 100 to 1000 times higher than material a. Detectors were made with the three samples. The results were shown in Figs. 6, 7, and 8. Fig. 6 shows the output signal of sample injections using different discharge types. Fig. 7 shows the plasma emission spectrum of a fused quartz tube. Fig. 8 shows the plasma emission spectrum of a synthetic quartz tube.

5.1 Calibration Curve (C12)

Fig. 9 shows the calibration curve for n-C12. The linear sensitivity range covers approximately 5 orders of magnitude (1 pg to 100 ng). The limit of detection estimated from the noise amplitude by the ASTM method is 0.3 to 0.6 pg C/sec. This confirms superior performance to FID (1.5 pg C/sec limit of detection).

5.2 Chlorine-Containing Samples and Alcohols

Fig. 10 shows the BID and FID chromatograms for a mixed sample of chlorine-containing samples and alcohols (10 ppm each component). FID exhibits low sensitivity for these compounds, whereas BID achieves sensitivity that favorably compares to hexane. FID achieves extremely low sensitivity to chlorine-containing samples, in particular. For example, the relative sensitivity of FID to chloroform is less than one-tenth its sensitivity to hexane, whereas little difference is apparent with BID.

5.3 Inorganic Gases

A comparison was made between BID and TCD measurements of inorganic gases that cannot be measured by FID. Fig. 13 shows the BID and TCD chromatograms for a gas mixture of hydrogen, oxygen, nitrogen, methane, and carbon monoxide (10 ppm each component). A measurement limit concentration applies to TCD but BID measurements achieve adequate SN ratio. BID achieves at least 100 times the SN ratio of TCD.
6. Conclusions

A discharge ionization detector was developed using atmospheric non-equilibrium plasma. The discharge stability of both-side dielectric barrier discharge and single-side dielectric barrier discharge were evaluated and a reduction in baseline output was achieved by suppressing impurities from the inner walls of the plasma generator. The relationship between the high-temperature characteristics of the charge collector insulator and the baseline fluctuations was revealed. Evaluation of the performance of the developed detector confirmed 1 pgC/sec max. limit of detection for n-C12 and a linear sensitivity range covering approximately 5 orders of magnitude. Comparison of BID results with FID and TCD measurement results on several standard samples confirms superior sensitivity to FID with respect to a mixed sample of chlorine-containing samples and alcohols and confirms that BID achieves at least 100 times the S/N ratio of TCD for inorganic gases.

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