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Dielectric Barrier Discharge Carbon Atomic Emission Spectrometer: Universal GC Detector for Volatile Carbon-Containing Compounds

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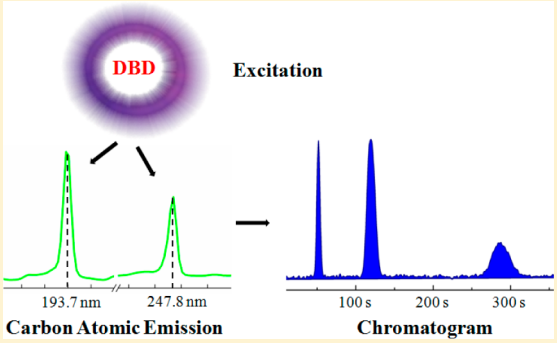
Supporting Information

ABSTRACT: It was found that carbon atomic emission can be excited in low temperature dielectric barrier discharge (DBD), and an atmospheric pressure, low power consumption, and compact microplasma carbon atomic emission spectrometer (AES) was constructed and used as a universal and sensitive gas chromatographic (GC) detector for detection of volatile carbon-containing compounds. A concentric DBD device was housed in a heating box to increase the plasma operation temperature to 300 °C to intensify carbon atomic emission at 193.0 nm. Carbon-containing compounds directly injected or eluted from GC can be decomposed, atomized, and excited in this heated DBD for carbon atomic emission. The performance of this new optical detector was first evaluated by determination of a series of volatile carbon-containing compounds including formaldehyde, ethyl acetate, methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol, and absolute limits of detection (LODs) were found at a range of 0.12−0.28 ng under the optimized conditions. Preliminary experimental results showed that it provided slightly higher LODs than those obtained by GC with a flame ionization detector (FID). Furthermore, it is a new universal GC detector for volatile carbon-containing compounds that even includes those compounds which are difficult to detect by FID, such as HCHO, CO, and CO_2. Meanwhile, hydrogen gas used in conventional techniques was eliminated; and molecular optical emission detection can also be performed with this GC detector for multichannel analysis to improve resolution of overlapped chromatographic peaks of complex mixtures.



Carbon is a component of all biological and botanical organisms, and most pollutants from various waters or the atmosphere are carbon-containing compounds. Therefore, sensitive and selective determination of volatile carbon-containing compounds in many environmental, clinical, and biological samples is frequently needed.[1] In fact, numerous methods including inductively coupled plasma-atomic emission spectrometry/mass spectrometry (ICP-AES/MS),[2−4] microwave induced plasma AES (MIP-AES),[5] glow discharge AES (GD-AES),[6,7] particle beam/hollow cathode glow discharge AES (PB/HC GD-AES),[8,9] direct current arc discharge AES,[10] and laser induced plasma AES[11,12] have been used for the determination of various carbon containing-compounds, such as nucleic acids,[9] amino acids,[13,14] protein[15] and carbohydrates[16] in soft drinks,[4] solid nuclear materials,[7] food,[17] water,[18] and environmental samples.[18,19] However, the direct determination of carbon by these AES methods is still challenging because it mainly emits in the vacuum ultraviolet region of the spectrum, which is absorbed by oxygen present in the large volume of the optical path.[20] Therefore, the vacuum condition or the inert gas-filled optical path is necessary to alleviate the adsorption by oxygen. However, these AES instruments are usually bulky and expensive, have high power consumption, and are difficult as portable instrumentation for field analytical chemistry.

Gas chromatography (GC) is usually applied for the analysis of volatile and semivolatile compounds and higher boiling point and more polar compounds with suitable derivatization. Although a great variety of GC detectors can be selected dependent on the analyte compounds, it is clear that elemental selectivity is a desirable characteristic. However, there exist several shortcomings to conventional element-selective detectors [e.g., the nitrogen−phosphorus detector (NPD) and the electron capture detector (ECD)] including limited application scope for several elements and low GC peak capacities from single channel detection. Despite that these problems can be solved to some extent with the application of MIP-AES or ICP-AES/MS as an excellent element-selective detector,[21,22] they

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are too expensive to be accepted in every laboratory and cannot easily meet the requirements of miniaturization for use as a GC detector. Therefore, it is still attractive to develop a more universal element-selective GC detector of compactness and low power consumption. A carbon optical emission GC detector is a relatively universal one for organic analytes and carbon-containing inorganic analytes such as CO, CO_2, and CS_2.

In contrast to conventional plasma such as ICP, MIP, and laser induced plasma (LIP), microplasma offers important advantages of simpler setup, lower power and gas consumption, field-portability, and convenient operation and has been extensively applied in various fields of analytical atomic spectrometry, such as capacitively coupled plasma (CCP)[23−28] and dielectric barrier discharge (DBD).[29−31]

DBD is a typical nonequilibrium gas discharge generated between two electrodes with a frequency of a few Hz to MHz and a voltage of 1−100 kV. It was first used as a miniaturized atomizer for the determination of halogenated hydrocarbons by diode laser atomic absorption spectrometry (DLAAS).[32] Due to its high molecular dissociation capability for production of various radicals, ions, atoms, and molecular fraction, DBD has also been used as an alternative to a traditional radioactive source (^{63}Ni foil) for ion mobility spectrometry (IMS),[33,34] as a source of soft ionization for mass spectrometry (MS),[35−38] or as a chemiluminescence (CL) GC detector based on reaction between DBD-split species and luminol.[39,40] In China, Zhang et al. pioneered the use of DBD in analytical chemistry including conventional atomic spectrometry,[41−43] ion source of mass spectrometry,[36,44,45] and imaging mass spectrometry.[46] Recently, Zhang et al. have proved that DBD could be used as a potentially alternative ablation mode to laser ablation for ICPMS for direct analysis of bulk material.[47] Most recently, we have successfully used DBD as a miniaturized radiation source to excite halohydrocarbons for generation of molecular emission of Cl_2^* (258 nm), Br_2^* (292 nm), and I_2^* (342 nm), which was very promising as a multichannel and element-specific GC detector.[48]

On the other hand, the energy for generation of atomic emission is generally much higher than that required for molecular emission,[49] but the gas temperature of DBD is about 600 K, much lower than that of an ICP (6000−10 000 K) or even of an air−acetylene flame (2000−3000 K). Not surprisingly, apart from the determination of mercury, DBD microplasma AES using a conventional design for sensitive determination of other elements has not been fully realized yet. Therefore, the purpose of this work is to construct a low power compact DBD microplasma carbon optical (atomic) emission spectrometer for determination of carbon-containing compounds after GC separation. To the best of our knowledge, this is the first report using a heated DBD coupled with a charge-coupled device (CCD) for optical quantification of carbon-containing compounds through carbon atomic emission measurements.

EXPERIMENTAL SECTION

Reagents. All chemicals used in this work were of at least analytical grade. Formaldehyde (HCHO, 40%), ethyl acetate ($CH_3COOCH_2CH_3$), methanol (CH_3OH), ethanol (CH_3CH_2OH), 1-propanol ($CH_3(CH_2)_2OH$), 1-butanol ($CH_3(CH_2)_3OH$), and 1-pentanol ($CH_3(CH_2)_4OH$) were purchased from Kelong Reagent Co. (Chengdu, China) and used as liquid carbon-containing compounds. Carbon monoxide (CO, 99.999%), methane (CH_4, 99.999%), and carbon dioxide (CO_2, 99.999%) were obtained from Qiaoyuan Gas Co. Ltd. (Chengdu, China) and used as carbon-containing gas compounds. Argon (Ar, 99.99%), helium (He, 99.999%), and nitrogen (N_2,99.999%) were also obtained from Qiaoyuan Gas Co. Ltd. (Chengdu, China) and tested as a discharge gas. Ar was also used as a carrier gas for the GC separation. Several wine samples were purchased from our local market.

Instrumentation. The whole instrumental setup was shown in Figure 1 and mainly consisted of a GC and the DBD-AES detector using a miniaturized CCD spectrometer. The cylindrical DBD device was housed in a laboratory-built heating box. The cylindrical DBD device was made according to our previous works.[48] Briefly, the cylindrical DBD device consisted of a quartz tube (50 mm × 3.0 mm i.d. × 5.0 mm o.d.) and two separated copper wires used as electrodes which were tightly wrapped around the outside of the tube evenly and inserted into the tube, respectively. The DBD plasma was generated when the two electrodes were connected to a compact ac ozone generation power supply (YG.BP105P, Electronic Equipment Factory of Guangzhou Salvage, Guangzhou, China; 6 cm long × 4 cm wide × 3 cm high, with a rated output of 4 kV, 20 kHz, and 12 W at 220 V, 50 Hz input). The ozone generation power supply was connected to a transformer (TPGC2J-1, Shanghai Pafe Electronic Equipment Ltd. Co., Shanghai, China) for convenient adjustment of the discharge power. Consequently, the characteristic atomic emission line of carbon at 193.0 nm was collected through the entrance slit of a commercial hand-held CCD spectrometer (Maya2000 Pro, Ocean Optics Inc., Dunedin, FL, USA) with a detectable spectral range from 176 to 400 nm. The practical resolution of this CCD spectrometer is about 0.4 nm. The CCD spectrometer was set about 3 mm to the observation window to alleviate the interferences arising from oxygen present in the air of the optical path. When it was used as a GC detector, it was directly connected to a Techcomp GC7890F GC instrument (Techcomp Ltd., Shanghai, China) equipped with a Rtx-Wax capillary column (30 m × 0.25 mm i.d, 0.50 μm polyethylene, Restek Co., Bellefonte, PA, USA) and a carbonaceous molecular sieve packed column (2 m × 4 mm i.d, Tianjin No.2 Chemical Reagent Factory, Tianjing, China) for analysis of the liquid samples and the gas samples, respectively.

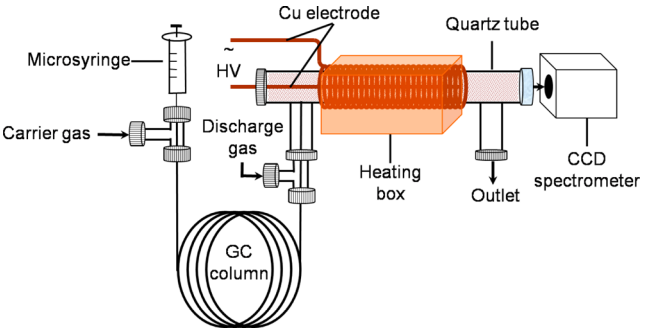

Figure 1. Schematic of the DBD-based carbon atomic emission spectrometer as a GC detector.

Analysis with Direct Injection. In the initial experiment, the carbon-containing compounds were directly analyzed to validate the carbon atomic emission from the DBD. These experiments were operated on a direct injection DBD-AES,

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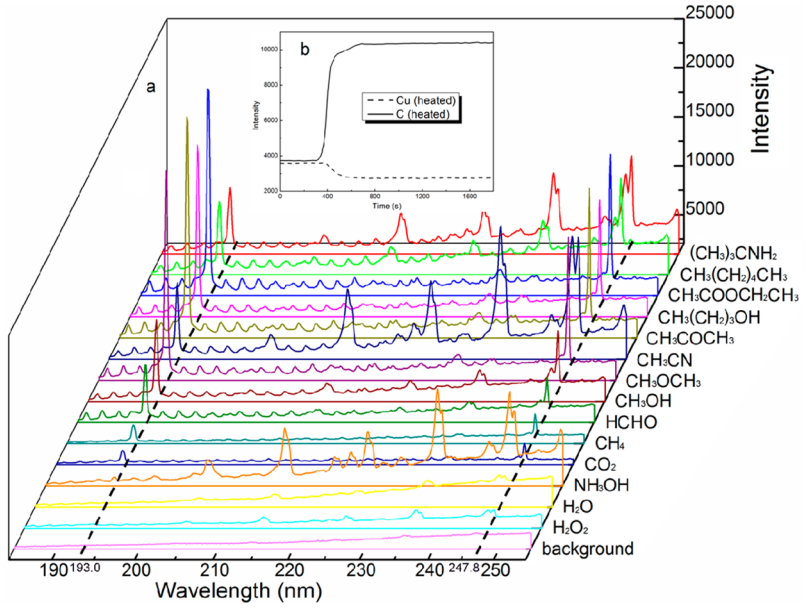

Figure 2. Identification of carbon atomic emission. (a) Carbon atomic emission at 193.0 and 247.8 nm from different compounds; (b) comparison of the responses of carbon atomic emission at 193.0 nm using a Cu inner electrode and a graphite electrode. Experimental conditions: discharge voltage, 2.95 kV; discharge gas flow rate, 300 mL min^{-1}; heating temperature, 300 °C; and CCD integration time, 100 ms.

which used a laboratory-built direct injection system to replace the GC of GC-DBD-AES in Figure 1. The system was composed of a 10 μL microsyringe and a 10 mL glass bottle heated by an electric jacket to 200 °C, as shown in Figure S1 (see the Supporting Information). An aliquot of 0.02 μL of each tested carbon-containing compound was separately injected into the heated vessel to generate the corresponding vapor and was further swept into the DBD plasma by the Ar carrier gas. Finally, the atomic emission of carbon at 193.0 nm was directly detected by the CCD spectrometer. A blank was measured by using the Ar carrier gas only.

DBD-AES as GC Detector. Both liquid and gaseous carbon containing compounds were used to evaluate the feasibility of the DBD-AES as a GC detector. An aliquot of 1 μL of liquid mixture containing HCHO, $CH_3COOCH_2CH_3$, CH_3OH, and CH_3CH_2OH and 1 mL of gaseous mixture containing 10% (v/v) CO, 20% (v/v) CH_4, and 20% (v/v) CO_2 were separately injected onto the Rtx-Wax capillary column or the carbonaceous molecular sieve packed column for separation and detection by the DBD-AES detector. For liquid sample, the inlet temperature was 300 °C; the Ar carrier gas was supplied at 2.0 mL min^{-1} in the constant-flow mode, and the temperature programming of the column started at 40 °C, was held for 2 min, then increased to 150 °C at a rate of 20 °C min^{-1}, was maintained for 2 min, and finally raised to 200 °C at a rate of 30 °C min^{-1} and held for 4 min. For gaseous sample, the inlet temperature was 60 °C; the Ar carrier gas was supplied at 40 mL min^{-1} in the constant-flow mode, and the oven temperature was programmed to start at 80 °C and held for 0.5 min, then increased to 120 °C at a rate of 20 °C min^{-1}, and held for 4 min.

RESULTS AND DISCUSSION

DBD has recently proven to be a promising miniaturized plasma as a portable atomizer or excitation source for hydride generation-AAS, atomic fluorescence spectrometry (AFS), AES, and molecular emission spectrometry (MES) as well as molecular MS.[50] As this is the first attempt to use DBD for

Table 1. Analytical Characteristics of the Proposed Method with Direct Injection

analyte	range (ng, as carbon)[a]	R^2	RSD (%, n = 6)	LOD (ng, as carbon)
HCHO	2–160	0.990	4.8	0.15
$CH_3COOCH_2CH_3$	2–180	0.998	5.5	0.19
CH_3OH	2–160	0.997	4.8	0.12
CH_3CH_2OH	2–160	0.999	2.2	0.15
CO	6–250	0.991	1.0	0.24
CH_4	4–150	0.992	0.9	0.28
CO_2	10–400	0.994	2.1	0.25

[a]Injection volume: 0.02 μL for liquid sample, 0.05 mL for gaseous sample.

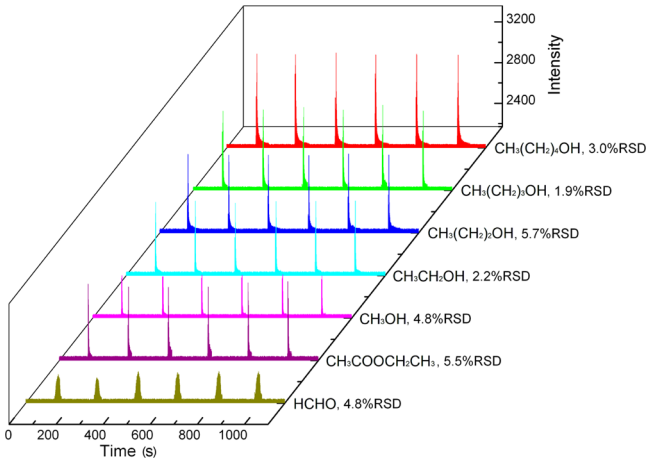

Figure 3. Stability of the carbon atomic emission at 193.0 nm from seven carbon-containing compounds. Experimental conditions: injection volume, 0.02 μL of pure analytes; discharge voltage, 2.95 kV; Ar discharge gas flow rate, 300 mL min^{-1}; heating temperature, 300 °C; and CCD integration time, 100 ms.

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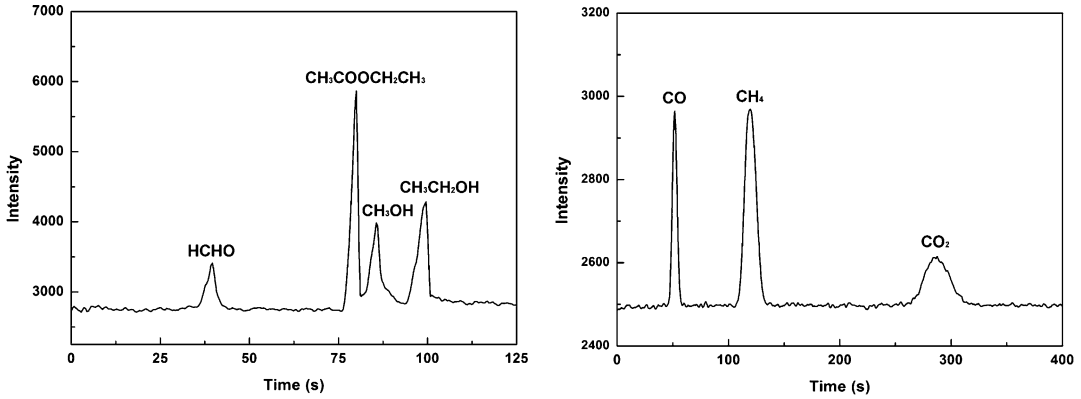

Figure 4. Chromatograms of carbon-containing compounds detected by the proposed GC detector under the optimized experimental conditions. Injection volume, 1 μL of a liquid sample (left) and 1 mL of a gaseous sample (right).

Table 2. Comparison of the Performance by the Proposed Method with FID

analyte	upper linear dynamic range, DBD (FID), ng (as carbon)	R^2, DBD (FID)	RSD (%, n = 6), DBD (FID)[a]	LOD, DBD (FID), ng (as carbon)
HCHO	100 (n.d.[b])	0.993 (n.d.)	4.6 (n.d.)	1.0 (n.d.)
$CH_3COOCH_2CH_3$	150 (60)	0.990 (0.9987)	2.6 (0.5)	1.2 (0.15)
CH_3OH	120 (50)	0.991 (0.9992)	4.7 (5.5)	0.8 (0.30)
CH_3CH_2OH	160 (70)	0.992 (0.9946)	1.6 (2.9)	1.1 (0.25)

[a]RSD, calculated at 20 μg mL^{-1}. [b]n.d., not detectable.

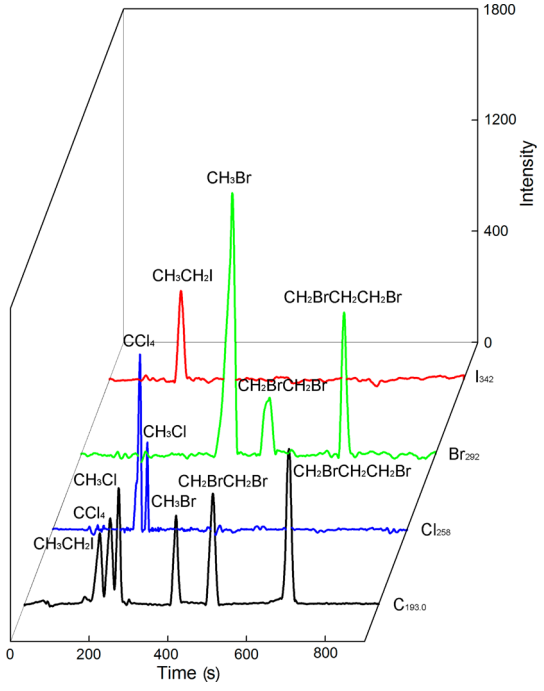

Figure 5. Chromatograms of a halohydrocarbon mixture detected by carbon atomic emission and halogen molecular emission under optimized experimental conditions. Injection volume, 1 μL.

atomic emission of carbon, it was necessary to undertake a detailed investigation of all influencing parameters on the emission characteristics.

Carbon Atomic Emission from DBD. Although DBD-MES has been used for determination of various molecules *via* monitoring their molecular emission bands,[48] the energy required for generation of atomic emission is generally much higher than that used for molecular emission. Specific atomic emission lines of carbon are usually generated in the plasmas with high temperature and high power consumption (i.e., ICP, MIP, and LIP) and CCP microplasma, while the DBD has rarely been used to generate atomic emission (e.g., mercury atomic emission).[24−27,42,51] Therefore, initial experiments were performed to indentify the feasibility of generation of specific carbon atomic emission in the DBD and the practicability as an element-specific detector for determination of carbon-containing compounds. Compared to the emission spectrum of the pure Ar DBD plasma, it is surprising that some obvious specific atomic emission lines of carbon at 193.0 and 247.8 nm were found when 0.02 μL of CH_3CH_2OH was injected into the heated vessel, with the peak widths of these emission bands of less than subnanometer, much narrower than the peak width of normal molecular/radical emission bands. Two approaches were used to further confirm that these atomic emission lines are related to carbon atoms. First, each compound with or without carbon including H_2O, H_2O_2, NH_3OH, CO_2, CH_4, HCHO, CH_3OH, CH_3OCH_3, CH_3CN, CH_3COCH_3, $CH_3(CH_2)_3OH$, $CH_3COOCH_2CH_3$, *n*-hexane, or *tert*-butylamine was used as an alternative to CH_3CH_2OH and injected into the DBD, respectively, with the results shown in Figure 2a.

Table 3. Recoveries of Four Carbon-Containing Compounds in Wine Samples

component	sample	spiked	found[a]	recovered (%)
HCHO, mg L^{-1}	93.8	50.0	134 ± 5.8	80
	93.8	250	298 ± 13	82
$CH_3COOCH_2CH_3$, mg L^{-1}	<1.2	50.0	42.0 ± 2.3	84
	<1.2	250	253 ± 6.6	101
CH_3OH, mg L^{-1}	<0.8	50.0	43.0 ± 1.6	86
	<0.8	250	233 ± 7.2	93
CH_3CH_2OH, g L^{-1}	9.01	0.25	9.27 ± 0.28	104
	9.01	2.50	11.3 ± 0.14	92

[a]Average ± standard deviation of three trials.

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Table 4. Comparison of the Analytical Results of Wine Samples Obtained by the Proposed Method and Those by GC-FID (in Parentheses)

component	sample 1	sample 2	sample 3	sample 4
HCHO, mg L^{-1}	194 ± 8.74[a]	93.8 ± 1.07	67.9 ± 3.11	n.d.
	(n.d.[b])	(n.d.)	(n.d.)	(n.d.)
$CH_3COOCH_2CH_3$, mg L^{-1}	n.d.	n.d.	n.d.	13.1 ± 0.15
	(1.22 ± 0.05)	(2.71 ± 0.1)	(0.723 ± 0.01)	(12.7 ± 0.28)
CH_3OH, mg L^{-1}	n.d.	n.d.	n.d.	n.d.
	(0.836 ± 0.04)	(0.949 ± 0.03)	(0.489 ± 0.01)	(0.531 ± 0.02)
CH_3CH_2OH, g L^{-1}	19.9 ± 0.54	9.01 ± 0.35	12.6 ± 0.38	22.8 ± 0.35
	(19.4 ± 0.23)	(9.64 ± 0.18)	(13.7 ± 0.41)	(19.5 ± 0.25)

[a]Average ± standard deviation of three trials. [b]n.d., not detectable.

The specific carbon atomic emission lines were always clearly observed when the injected analyte was a carbon-containing compound, while these emission lines did not appear when any of the noncarbon-containing compounds (H_2O, H_2O_2, and NH_3OH) was injected. Second, a graphite electrode was selected to replace the inner copper electrode, and then, a comparison of the emission spectra obtained from the cylindrical DBD using the inner copper electrode and the graphite electrode was made, as shown in Figure 2b. Not only the DBD with graphite electrode but also that with copper electrode can emit the weak carbon atomic emission in the beginning of the ignition of the plasma. However, the signal with the copper electrode decreased quickly to background level; in contrast, the signal from the graphite electrode increased significantly with the operation time, followed by a plateau at longer time. The initial spectral signal from the copper electrode may be attributed from the residual organic compounds on the surface of the inner electrode and thus disappeared when the organic compounds were burned up. Compared to the previous works using other high temperature plasmas as excited sources,[3,13] the emission lines at 193.0 and 247.8 nm were further confirmed to be carbon atomic emission, with the former more sensitive and spectrally clean.

Although DBD plasma has been used as excitation source for determination of mercury and some organic substances by atomic emission spectrometry and molecular/radical emission spectrometry, respectively, the mechanism of atomization and excitation of elements with DBD is still unclear because of its complicated nature of the plasma process. On the basis of the previous works and the observed atomic emission lines (193.0 and 247.8 nm) of carbon, we speculate that the mechanism of the proposed work may involve the following steps: (1) carbon containing compounds are first dissociated to carbon atoms (C) by high energetic electrons in the DBD Ar plasma; (2) the high energetic electrons and the excited argon atoms (Ar^m) excite the generated carbon atoms to their excited states (C*); and (3) the atomic emission lines at 193.0 and 247.8 nm are observed when C* excimer atoms release their excitation energy and relax to the ground state.[52−54] Moreover, the deep UV (126 nm) emitted from DBD atomizer may also contribute to the dissociation of the carbon-containing compounds and/or generating C* excimer atoms due to their powerful capability in decomposition of organic pollutants.[48] It is worthwhile to note that the heated DBD environment is helpful in keeping the analyte gaseous state, which is beneficial to the atomic emission and enhances the sensitivity through consuming less energy for gasification.

Optimization of Operation Parameters for DBD. It is well-known that the type and flow rate of discharge gas strongly affect the analytical application of DBD. In this work, three different gases, including Ar, He, and N_2, were tested as the discharge gas to investigate the effect of carrier gas on the spectral response, with the results similar to those reported earlier for DBD-AES (Figure S2, see the Supporting Information). All the tested gases could maintain the DBD plasma easily and provided several typical emission bands of OH (283, 309 nm), N_2 (358, 380 nm), CN (387 nm), and NH (337 nm), in agreement with the reported results obtained from DBD plasma or other different type plasmas. It can be seen that no emission lines around 193.0 nm were observed regardless of the type of discharge gas, so it can be used as a background spectrum. The atomic emission of carbon (193.0 nm) was too weak to be used for analytical application in the case of nitrogen as the discharge gas when CH_3CH_2OH was injected. This is probably due to the excitation energy of N_2 plasma being much lower than that arising from Ar or He plasma.[41] Both He and Ar plasma can be used as discharge gas for efficient excitation of carbon atomic emission, and Ar was selected as the discharge gas for the subsequent experiments because it is cheaper than He. Argon acted as not only the discharge gas for plasma but also the carrier gas to transfer the analytes to the DBD plasma. Figure S3a (see the Supporting Information) shows that the spectral responses from seven carbon containing-compounds decreased significantly with the flow rate of Ar throughout the range of 300−900 mL min^{-1}. Lower Ar flow rate resulted in inefficient generation of DBD plasma and low efficiency of analyte transport to the DBD detector; higher flow rate resulted in significant dilution of analyte in the carrier gas. Therefore, a transport gas flow rate of 300 mL min^{-1} was selected for all further experiments.

The DBD plasma is ignited and fills in the DBD device when a high voltage is applied between the two copper electrodes. Therefore, the investigation of the effect of discharge voltage on spectral response was also undertaken, and the results were summarized in Figure S3b (see the Supporting Information). A signal plateau for each analyte compound was obtained in the range of 2.5−4 kV. Lower discharge voltage cannot generate and maintain the plasma steadily, while the two electrodes could be etched much faster and the plasma cannot remain steady at higher voltage. Therefore, both higher and lower discharge voltages result in a less intensive and less steady plasma process, thus decreasing the response. A discharge voltage of 2.95 kV was chosen for subsequent measurements in this work.

As mentioned earlier, the low power DBD plasma has been used for atomization of only hydrides and excitation of molecules or a few kinds of atoms such as mercury. As expected, the initial results showed that the carbon atomic

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emission resulting from HCHO, CH_3OH, CH_3CH_2OH, $CH_3(CH_2)_2OH$, $CH_3(CH_2)_3OH$, or $CH_3(CH_2)_4OH$ in the room temperature DBD plasma was found to be very weak and thus have low sensitivity. Interestingly, however, the carbon atomic emission significantly increased several fold when the DBD device was heated, as shown in Figure S3c (see the Supporting Information). The relation between the carbon atomic emission intensity and the operation temperature was further carefully investigated, with results summarized in Figure S3d (see the Supporting Information). All responses from the analyte compounds increased with an increase in the operation temperature throughout the range of 60−250 °C. Then, the responses slightly increased or were steady at higher temperature. These results implied that higher temperature mainly helped volatilization of the analytes and avoided extra consumption of the energy extracted from the DBD plasma. Unfortunately, our DBD device cannot endure higher temperature because the silica gel used to seal the DBD device is fused when the temperature is higher than 300 °C. An operation temperature of 300 °C was, therefore, chosen for subsequent experiments.

Analytical Characteristics of DBD Detector with Direct Injection. Under optimal conditions, the analytical figures of merit were evaluated by direct injection of 1 μL of liquid samples (HCHO, $CH_3COOCH_2CH_3$, CH_3OH, and CH_3CH_2OH) or 1 mL of gaseous samples (CO, CH_4, and CO_2), with the results summarized in Table 1. The peak area measurement was recorded for a wider linear dynamic range. The linear correlation coefficients of determination for calibration curves were better than 0.99 for all carbon-containing compounds tested at trace concentration level but began to deviate from linearity at concentrations >300 ng due to insufficient excitation power of the DBD for higher analyte concentrations. The limit of detection (LOD), which is defined as the analyte concentration equivalent to three standard deviations of 11 measurements of a blank solution, was better than 0.12 and 0.28 ng for liquid and gaseous carbon-containing compounds, respectively. The precision, which is expressed as relative standard deviation (RSDs) of six replicate measurements, was better than 6% for all of the tested compounds at 1 μL of analyte (Figure 3). These figures of merit are comparable or better than those of similar analytical methods, as summarized in Table S1 (see the Supporting Information).

DBD-AES as GC Detector. The DBD-AES carbon detector could be a universal GC detector for determination of carbon-containing compounds. To reduce the dead volume, the DBD cell should be coupled to the GC as close as possible. The performance of the DBD-AES as a GC detector was investigated with a liquid mixture containing CH_3OH, CH_3CH_2OH, HCHO, and $CH_3COOCH_2CH_3$ and a gaseous mixture containing CO, CO_2, and CH_4. The typical chromatograms were shown in Figure 4. The results indicate that all the tested compounds including those undetectable by the flame ionization detector (FID) (CO, CO_2 and HCHO) can be detected with satisfactory sensitivity. The analytical figures of merit of the proposed technique were compared with those by GC-FID (Table 2). The linear coefficients of calibration curves were better than 0.99. The absolute LOD was found to be in the range from 0.8 to 1.2 ng. It should be noted that the sensitivity and absolute LOD could be further improved to be comparable to those by GC-FID if the serial dilution of analytes by high flow rate discharge gas is minimized by reducing the inner diameter of the discharge tube. Meanwhile, they can also be significantly improved when a photomultiplier tube (single channel) or a intensified CCD spectrometer is used for optical detection.

A CCD spectrometer not only has the advantage of campactness but also has simultaneous multichannel capability. Therefore, this DBD-CCD-based GC detector can also be used for simultaneous multichanel detection of both carbon atomic emission and molecular emission of analytes.[48] It can be expected that this GC detector not only provides universal detection of all carbon containing compounds but also further offers advantage of multichannel simultaneous analysis for improved resolution of overlapped chromatographic peaks of complex mixtures. A mixture containing chlorinated hydrocarbons (CCl_4 and CH_3Cl), brominated hyrocarbons (CH_3Br, CH_2BrCH_2Br, and $CH_2BrCH_2CH_2Br$), and iodinated hydrocarbons (CH_3CH_2I) was used to demonstrate this hypothetical superiority, as shown in Figure 5. All the tested analytes could be detected when the chromatogram was run on the C 193 nm, but CH_3CH_2I, CCl_4, and CH_3Cl could not be completely baseline-resolved. In contrast, these tested analyte peaks appear completely resolved when other detection channels of the CCD spectrometer were set at 258, 292, and 342 nm to monitor the molecular emission of Cl_2^*, Br_2^*, and I_2^* arising from chlorinated hydrocarbons, brominated hydrocarbons, and iodinated hydrocarbon, respectively; thus, high resoultion detection for the complex sample is possible.

Samples Analysis. A wine sample was analyzed to preliminarily show the potential application of the proposed technique. A series of standard solutions containing various concentrations of HCHO, $CH_3COOCH_2CH_3$, CH_3OH, and CH_3CH_2OH were used to construct a calibration curve. The peak area was recorded for the quantification of these analytes with external standard calibration. It was necessary to spike the sample with $CH_3COOCH_2CH_3$ and CH_3OH because their endogenous concentrations were below the detection limits. Furthermore, a significant 500-fold dilution of the sample with DIW was required prior to determination of CH_3CH_2OH because their concentration exceeded the linear range. The analytical results were summarized in Table 3. The recoveries for HCHO, $CH_3COOCH_2CH_3$, CH_3OH, and CH_3CH_2OH were from 80% to 104%. A comparison between the analytical results of several wine samples obtained by the proposed method and GC-FID was made and summarized in Table 4. Both methods were performed on the same GC instrument with identical parameters. Although the low concentration level of $CH_3COOCH_2CH_3$ and CH_3OH can be easily determined by GC-FID, the concentration of HCHO can be determined only by this proposed method since no signal of HCHO arose from GC-FID.

CONCLUSIONS

In conclusion, carbon atomic emission was found in low temperature DBD, and the emission signal can be dramatically enhanced by heating the DBD tube. The finding was used to design a new GC detector for carbon-containing volatile compounds. This GC detector has many advantages: (1) universality for volatile organic compounds; (2) capability for detection of HCHO, CO, and CO_2, which are not detectable by GC-FID; (3) possible simultaneous multichannel analysis for improved resolution of overlapped chromatographic peaks of complex mixtures, together with simultaseous use of molecular emission; and (4) simplicity, atmospheric operation, compactness, high resolution, cost-effectiveness, and low power

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consumption. With the accomplishment of DBD-AES for other elements of compounds, the proposed technique should have even wider applications.

■ ASSOCIATED CONTENT

Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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