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Capacitively coupled microplasma for on-column detection of chromatographically separated inorganic gases by optical emission spectrometry

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Abstract

Two tubular electrodes placed on a capillary tubing are used to couple an electrical ac field of high voltage (20 kV) but low frequency (20 kHz) and about 8 W power inside for generation of the plasma. The emitted radiation is passed to a spectrometer via an optical fibre butted to the side of the capillary. The excitation temperature of the plasma determined from helium emission lines is about 4000 K. It was found possible to detect oxygen from its emission at 777 and 845 nm, hydrogen at 656 nm and sulfur containing species from emission at 923 nm. The carbon-containing species CH_4, CO, and CO_2 could be determined from an emission band at 385 nm due to CN. Detection limits in the range between about 1 and 10 ng were obtained using a miniature diode array spectrometer.
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Keywords: Detection, GC; Optical emission spectrometry; Capacitively coupled microplasma; Gases

1. Introduction

Optical emission spectrometry with a plasma radiation source has shown several advantages as detection method in gas chromatography. It is element specific, has a good dynamic range and high sensitivity. The standard plasma detector is the microwave-induced plasma (MIP) system [1]. However, this type of plasma needs a special, relatively bulky, cell geometry and an impedance matching system for coupling the microwave generator with the plasma cavity. It has a power consumption of about 100 W, requires several litres of helium per minute as make-up gas and in general needs a Tesla discharge system for start up.

In an effort to overcome these disadvantages, several alternative plasma systems for detection in gas chromatography have been reported in recent years. Blades and coworkers demonstrated the use of a capacitively coupled plasma based on parallel plates and operated with 13.56 or 27.18 MHz and typically 50 W of power constructed on a rectangular quartz tube of a cross-section of 2 mm × 4 mm and 80 mm length and reported the determination of organotin compounds [2,3]. Quan et al. [4] evaluated a small extra column detector based on two perforated disk-shaped electrodes in direct contact with the gas. The plasma is generated by applying 5 W of radiofrequency power which requires impedance matching. It is sustained by the helium carrier gas mixed with an auxiliary flow of oxygen. This system shows a detection limit to chlorine (sample as hexachlorocyclohexane) of 8.5 pg.

Schepers and Broekaert proposed a direct current hollow cathode glow discharge (HCGD) system as extra-column GC detector [5]. It has a power consumption of about 20 W and a gas consumption of 5 ml min^{-1} of Helium. This detector works at reduced pressure and therefore needs a vacuum pump system. It shows a detection limit of 5 pg s^{-1} to chlorine and 3 pg s^{-1} to bromide, sample as 1-bromo-3-chloropropane.

Manz and coworkers [6] introduced a miniature direct current microplasma on a microfabricated chip. It had a volume of 50 nl and worked at reduced pressure. The distance between the electrodes was between 2 and 5 mm. It showed a detection limit of 3 pg s^{-1} to methane, but had a lifetime of only 2 h because of the sputtering of the cathode material. Subsequently these workers [7,8] improved the plasma on chip to work at atmospheric pressure and and with an

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extended lifetime of more than 24 h. This dc microplasma had a power consumption of 9 mW and a gas consumption of 0.019 ml min^{-1} of helium. It showed a detection limit of 1 pg s^{-1} to hexane.

Pedersen-Bjergaard et al. [9–13] proposed a radiofrequency plasma, operated at 350 kHz and sustained inside the end of a capillary column (0.25 μm, i.d.). The plasma generation system consisted of two electrodes; one in the shape of a ring on the outside of the capillary column and the other at its end in direct contact with the gas. This system could be maintained with 25 W and a gas flow between 1.5 and 5 ml min^{-1}. It showed a detection limit of 1.1 pg s^{-1} to chlorine.

The microplasma employed in this work is a low-frequency (20 kHz) ac plasma of high voltage (20 kV) [14]. Impedance matching is not necessary at this frequency. Both electrodes are tubular and placed outside the capillary. The energy is capacitively coupled into the tube and because of the physical separation sputtering of the electrodes and contamination of the plasma does not occur. Micromachining is not needed and as the atmospheric pressure plasma is created on the column there is no dead-volume nor is a make-up gas required. The detection of the inorganic gases explored in this project is of industrial importance. The non-combustable ones do not show a response in the flame ionization detector, and hydrogen is not detectable by thermal conductivity measurement.

2. Experimental

Schematic drawings of the overall system and the detector are shown in Fig. 1. The separation system consists of a commercial capillary chromatograph with split injector (HRGC mega 2 series, Carlo Erba, Valencia, CA, USA) equipped with a microvolume thermal conductivity detection (TCD) system (Vici, Houston, TX, USA) and followed by the purpose-built on-column plasma detector. The latter is based on 2 cylindrical electrodes of ca. 1 cm length each, cut from hypodermic needles (Neolus No. 14, Terumo, Leuven, Belgium) and fitted on fused silica tubing (250 μm i.d. × 350 μm o.d., BGB Analytik, Anwil, Switzerland) and separated by 1 cm. Each electrode is held in place with a clamp made from brass which serves to make the electrical connections and the clamps in turn are mounted in insulating ceramic blocks kept aligned with a spacer made from perspex. Power to the plasma cell is provided with a purpose made ac-high voltage generator delivering 20 kV at 20 kHz. The plasma is self-igniting. A ceramic block with appropriate holes serves to butt an unterminated optical fibre (200 μm i.d., type FG-200UEP, Thorlabs, Newton, USA) in a 90° angle to the outside of the capillary. The other end of the fibre was terminated with an SMA connector and brought to a miniature portable diode array-spectrometer (S2000 from Ocean Optic, Florida, USA, spectral bandwidth: 1.85 nm; integration time : 3 ms) connected to a personal computer for monitoring the plasma emission. The spectrum of Fig. 2 was acquired with a MS 260i charge-coupled device (CCD) spectrograph from Oriel (Stratford, CT, USA, spectral resolution 0.10 nm). The TCD signal was collected with a MacLab/4e data acquisition system (ADInstruments) and a Macintosh computer (Apple, Cupertino, CA, USA). Note that the plasma detector is designed to be placed directly on the end of a separation capillary. In this case however, it was fitted with a separate piece of capillary spliced to the outlet of the micro-TCD system in order to allow comparative measurements.

Helium (99.9999%, Carba Gas, Basel, Switzerland) was used as carrier gas. A molecular sieve column (Molesiv,

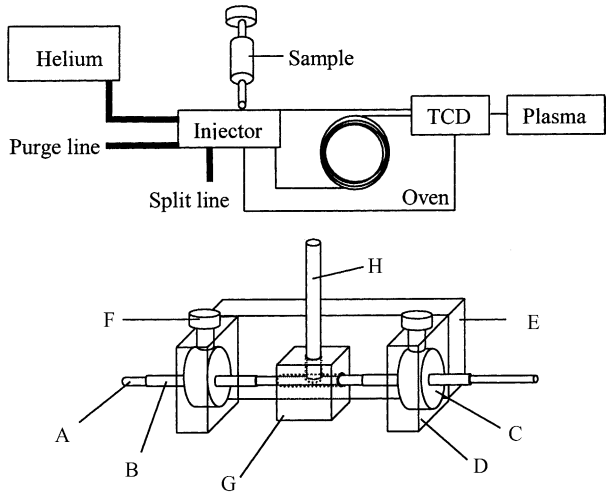

Fig. 1. Sketch of the experimental set-up. Top: chromatographic system with two detectors in series. Bottom: detector cell. (A) Fused silica tubing, (B) electrodes, (C) brass connector to the electrodes, (D) ceramic electrode holder, (E) Perspex spacer, (F) electrical connections, (G) ceramic holder (10 mm × 10 mm × 10 mm) for optical fibre, (H) optical fibre.

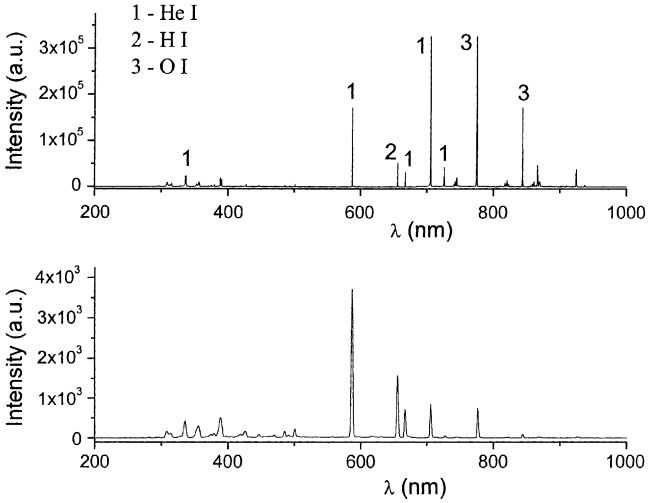

Fig. 2. Emission spectra for a helium blank using a hydrocarbon coated separation capillary. Top: acquired with high resolution spectrometer. Bottom: collected with portable spectrometer.

30 m × 0.53 mm, J&W Scientific, Folsom, CA, USA) was used for the separation of hydrogen, oxygen and nitrogen, while a carbohydrate column was employed for the other gases (Carboxen 1006, 30 m × 0.53 mm, Supelco, Buchs, Switzerland). The flow rates were 4 ml min^{-1} (carrier), 40 ml min^{-1} (split line) and 12 ml min^{-1} (septum purge). The injection was performed with either a 4, 10 or 50 μl syringe. Further chromatographic parameters were: injector 80 °C, oven 40 °C and detector (TCD) 170 °C (when using the molecular sieve column); injector 110 °C, oven 110 °C, detector 170 °C (Carboxen 1006 column) and injector 110 °C, oven 200 °C, detector 210 °C (Carboxen 1006, SO_2-determination).

The gas standards and samples were prepared by mixing and dilution in helium or air by using mass flow controllers (Type 1179A and 1159B, with maximum flow rates of 10, 20, 100 and 200 ml min^{-1}; MKS Instruments, Munich, Germany), a gas sampling bulb with stopcock (125 ml, Supelco). Compressed helium (99.9999%), carbon dioxide (99.99%), methane (99.99%), carbon monoxide (99.9%) sulfur dioxide (99.9%) nitrogen dioxide (99.9%), air (99.99%) and hydrogen (99.99%) was provided by Carba Gas.

3. Results and discussion

The plasma can be sustained at atmospheric pressure in helium for flow rates between about 3 and 200 ml min^{-1} which well encompasses carrier flow rates used in most capillary chromatographic methods. At lower flow rates the silica capillary is not adequately cooled, which will result in its melting. With care however, the same capillary may be employed for several months.

Blank emission spectra obtained with the helium carrier gas are given in Fig. 2. The spectrum at the top was collected with a desktop high resolution spectrometer while the bottom one was obtained with a compact portable spectrophotometer (focal length 42 mm). The plasma temperature as was obtained from a Boltzmann plot of the helium intensities recorded with the high resolution spectrometer (388.9, 471.3, 492.2, 501.6, 587.6, 667.8, 706.5 and 728.1 nm) [15] and calculated to be about 4200 K (with an estimated uncertainty of at least ±20% due to varying spectral sensitivities of the detector and transmission losses in the fibre). Note that in our previous publication [14] a temperature estimated as about 12,000 K was reported. The difference is thought to arise from the different geometrical arrangement used in the positioning of optical fibre (previously it was inserted axially into the capillary) and indicates a geometrical inhomogenuity of the plasma. Considering that in comparison to the well know inductively coupled plasma, the physical dimensions of the cell, the gas flow rate and the power all scale by approximately a factor of 100, the power density in both plasmas is comparable and the temperatures can be expected to be similar. A dependence of the spectrum on the flow rate of helium was observed. For the chromatograph employed, this was dependent on the temperature of the column oven (6.7 ml min^{-1} at 40 °C, 4 ml min^{-1} at 110 °C and 3.3 ml min^{-1} at 200 °C), which hence indirectly alters the plasma temperature by about 1000 K. Note, that besides emission from helium also pronounced lines from oxygen and hydrogen could be identified in the blank. The oxygen lines are also present when the plasma is operated directly from a helium supply (i.e. without the chromatographic column) and oxygen may either be present as impurity in the helium supply or possibly originate from entrained air. The weak line at 656 nm ascribed to hydrogen was found to be much reduced when using a molecular sieve column in place of the hydrocarbon coated column employed in the acquisition of the spectra shown in Fig. 2. This may indicate bleeding of material from the stationary phase when using the hydrocarbon column.

Clearly, band broadening and spectral overlaps are evident for the lower resolution spectrometer as evidenced in the bottom spectrum of Fig. 2. Nevertheless, the resolution was adequate for the monitoring of the lines used in the acquisition of chromatograms. It was found that O_2 was best monitored at 845 or 777 nm and H_2 at 656 nm. These lines correspond to the atomic species and are identical to the ones observed when using the conventional MIP [1]. Carbon containing species (CO, CO_2 and CH_4) all yielded an emission line at 385 nm. By investigating this line with the high resolution spectrometer it could be determined to be at 385.2 nm and to belong to the structure of the CN-violet band [16]. The species must be formed with nitrogen thought to present (along with oxygen) as impurity in the plasma gas. Atomic carbon emission might be present at 193 nm and nitrogen emission at 174 nm, the lines usually employed with the MIP for these species [1]. However, wavelengths below about 240 nm are not accessible with our systems, due to losses in the optical fibres. It was not possible to find an emission line for nitrogen in the accessible wavelength range. This is not entirely unexpected as sensitive lines for non-metals outside the UV range are rare also for the inductively coupled plasma (see for example ref. [17–19]). Another species of interest is SO_2, which with a MIP leads to an emission line for atomic sulfur at wavelength = 180 nm [1], also not accessible with our detector. The most sensitive accessible sulfur line was found to be in the near infrared range at 923 nm. The emission lines used for carbon at 385 nm and for sulfur at 923 nm as monitored during the passage of a chromatographic peak are illustrated in Fig. 3. Note the presence of peaks belonging to the background in the vicinity of the CN band.

Chromatograms obtained with a molecular sieve column at 40 °C following a single injection of a sample of hydrogen (approximately 80%) in air are shown in Fig. 4. Several wavelengths were monitored concurrently along with the signal from the standard TCD system. It was found that hydrogen could be detected readily with the new detector by monitoring its emission line at 656 nm, while no signal is present for this species with TCD because of the similarity

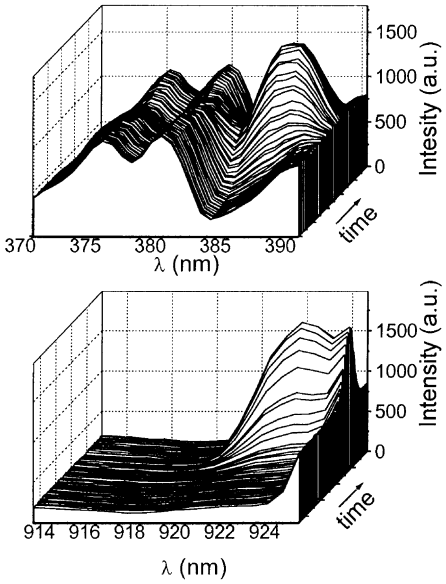

Fig. 3. Emission spectra acquired during passage of a peaks. Top: CH_4, Bottom: SO_2.

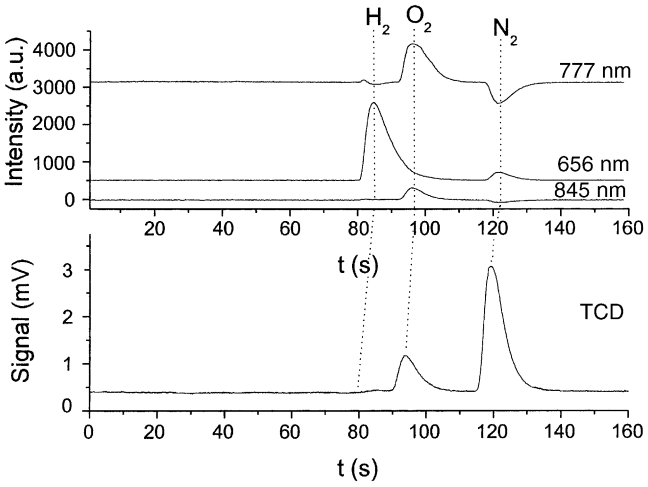

Fig. 4. Chromatograms for hydrogen in air. Top: plasma detection at three different wavelengths, Bottom: TCD.

of the thermal conductivity of hydrogen with that of the carrier gas helium. Oxygen could be detected at 777 and 845 nm with different sensitivities on top of a background signal due to the presence of oxygen as impurity. Nitrogen,

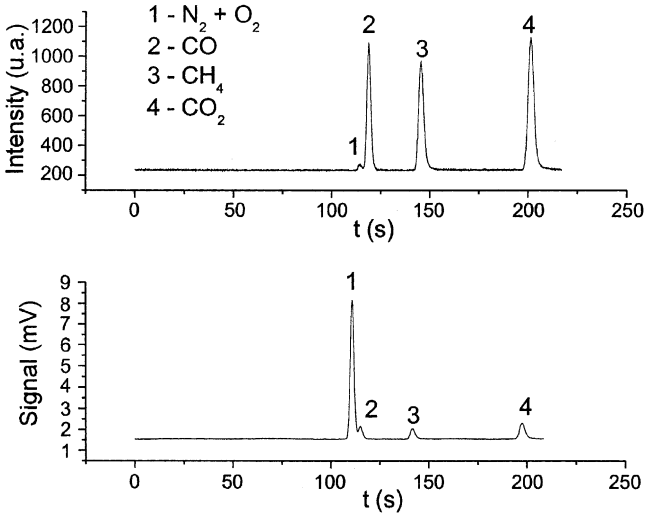

Fig. 5. Chromatograms for CO, CH_4, CO_2 in air. Top: plasma emission intensity at 385 nm. Bottom: TCD.

for which there is no available emission line, was found to cause a disturbance of the background intensity for oxygen. The reason for this is not clear, but the feature might be employed for indirect determination of nitrogen. The mass detection limits for oxygen and hydrogen were determined as 2 and 14 ng, respectively. Further performance data is summarized in Table 1.

A mixture of CO, CO_2 and CH_4 in air was then separated on a hydrocarbon coated capillary column at 110 °C, because the molecular sieve column used previously is not suitable for the mixture. As stated above, at the higher oven temperature the blank helium emission spectrum has some differences, notably the emission line to H (656 nm) shows a higher baseline value. It was also observed that the O emission line (777 nm) is noisier than at the lower oven temperature. In this case all three species lead to peaks in the TCD chromatogram, as do nitrogen and oxygen which show up as a single peak illustrated in Fig. 5. The carbon containing species can be monitored via the emission band from the plasma at 385 nm with better sensitivity. The mass detection limits (3 × S.D.) obtained for CO, CO_2 and CH_4 with the plasma detector are 2.7, 1.9 and 0.3 ng respectively, while the corresponding values for CO_2 and CH_4 obtained with TCD are 20 and 9 ng, respectively. The detection limit for

Table 1
Calibration data and detection limits

	TCD				Plasma				
	Range (ng)	R^2	DL (ng)	DL (%)	λ (nm)	Range (ng)	R^2	DL (ng)	DL (%)
H_2	–	–	–	–	656	–	–	14	–
O_2	30–120	0.996	7.5	–	777	30–120	0.9993	2	–
CH_4	30–160	0.9865	9	2.5	385	5–210	0.9822	0.2	0.06
CO_2	200–500	0.9883	20	2.0	385	20–500	0.9899	1.9	0.19
CO	–	–	–	–	385	20–100	0.9687	2.7	0.43
SO_2	–	–	–	–	953	100–400	0.9974	9.0	0.32
NO_2	1000–4000	0.9959	35	3.4	777	1000–4000	0.9973	87	8.47

Table 2
Determination of CO, CH_4 and CO_2 in four artificial samples

Sample	CO (ng) injected	CO (ng) determined	S.D.	CH_4 (ng) injected	CH_4 (ng) determined	S.D.	CO_2 (ng) inejcted	CO_2 (ng) determined	S.D.
G1	24.0	20.5	0.9	15.6	16.7	0.2	42.5	37.2	0.7
G2	50.6	48.2	0.3	36.0	36.7	0.2	104.0	106.2	0.8
G3	74.8	74.6	0.7	31.4	31.6	0.1	128.6	136.6	0.5
G4	46.3	47.3	0.3	38.1	38.1	0.1	104.1	108.1	1.2

S.D. = absolute standard deviation ($n = 5$).

CO with TCD was not determined because of the limited resolution from the peak for air (see bottom chromatogram of Fig. 5). Calibration curve data is given in Table 1. The reason for the small peak for air with the plasma at the wavelength employed is not understood. Four artificial samples of mixtures of the three species were then prepared and analysed to further validate the method. The recovery was generally found to be good. The detailed data are given in Table 2.

The determination of SO_2 using the emission line for atomic sulfur at 923 nm was then investigated. To achieve the elution of SO_2 within a reasonable span of time, the oven temperature was increased to 200 °C. A chromatogram of a SO_2 sample can be seen in Fig. 6. The detection limit was determined as 9 ng. An inspection of the chromatogram for SO_2 obtained with TCD (bottom trace of Fig. 6) illustrates that also in this case the detection limit obtained with the plasma is better.

Also studied was the determination of NO_2 in air. As stated previously, no emission signal to nitrogen could be observed in the spectral working range from 250 to 1000 nm accessible with our system, therefore the oxygen line at 777 nm was employed. The resulting chromatogram is shown in Fig. 7 along with the TCD trace. The first peak in both chromatograms is the one to air, which shows the negative going deviation noted above in the oxygen intensity on passage of nitrogen. In this case the sensitivity when monitoring the oxygen emission from the plasma (see Table 1) was not quite as good as that obtained with TCD.

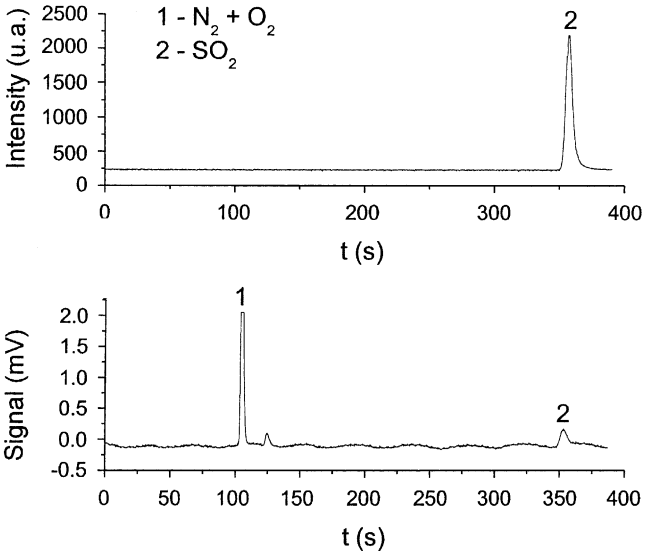

Fig. 6. Chromatograms for SO_2 in air. Top: plasma emission intensity at 922 nm. Bottom: TCD.

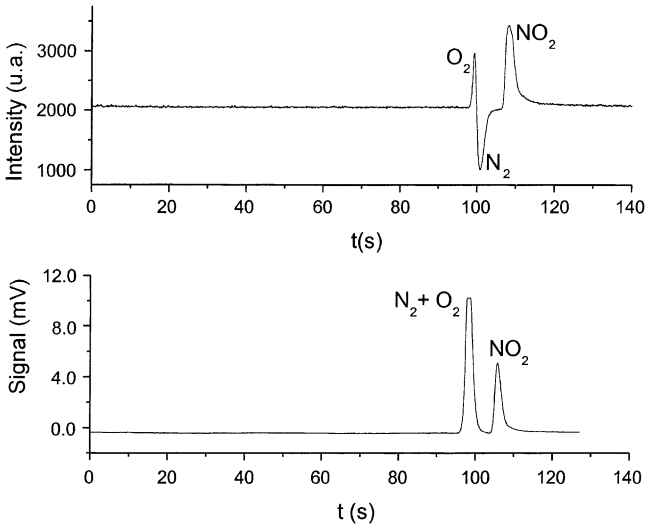

Fig. 7. Chromatograms for NO_2 in air. Top: plasma emission intensity at 777 nm. Bottom: TCD.

4. Conclusion

The microplasma was found to allow the determination of inorganic species with sensitivities which are comparable or better then those achieved with conventional thermal conductivity detection, the common method for these gases. The spectral selectivity of the new detector imparts additional information on the peak identity, or may allow the resolution of otherwise overlapping peaks (as in the determination of CO in air reported above). As a small diode-array based spectrometer provides adequate resolution, the overall detection system is inexpensive, compact and requires little power. These features render the detector a suitable alternative for portable gas-chromatographs, which are commonly equipped with a thermal conductivity detector. Note that the concentration detection limits for the gaseous species (these are approximately 0.5% (v/v) in the gas phase) are not adequate for trace determinations in environmental monitoring, but should be suitable for industrial applications.

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