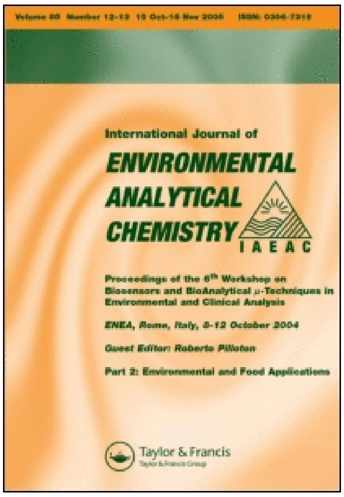

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# Element Specific GC-Detection by Plasma Atomic Emission Spectroscopy—A Powerful Tool in Environmental Analysis

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# ELEMENT SPECIFIC GC-DETECTION BY PLASMA ATOMIC EMISSION SPECTROSCOPY—A POWERFUL TOOL IN ENVIRONMENTAL ANALYSIS*

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A new Plasma Emission Detector (PED) to be used in gas chromatography has been developed, consisting of a capacitively coupled helium plasma operating at 200 W and 27 MHz and a polychromator system. Elements such as H, C, N, O, S, F, Cl, Br and I can be simultaneously detected, giving way to new possibilities of measuring organic environmental pollutants.

1. Non-separated compounds can be easily measured with the PED, as long as the compounds contain different hetero-elements.
2. The calibration for a complex system as for example the chlorinated HC's demands only for a single standard.
3. The simultaneous detection of all elements of a separated compound allows the calculation of the total molecular formula.

The detection limits for different elements lie between 50 and 200 pg/sec at a signal to noise ratio of 3 to 1.

KEY WORDS: GC detector, plasma emission detector, element specific detector, SCP, stabilized capacitative plasma.

## INTRODUCTION

The continuous developments in instrumental analysis helped to bring many environmental problems to the surface and to point out ways to solve them. For example old industrial waste deposits may contain more than 100 000 possible water-contaminating compounds. There are other thousands of possible degradations products and metabolites in addition. All these chemicals, menacing water, soil and air, cannot be measured all by themselves. In the future more than ever the determination of so called "guiding chemicals" will be necessary. Nevertheless, very selective analysis methods are needed to keep interferences in a determination

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as low as possible. Apart from spectrometric and chromatographic methods so called hyphenated methods have become important during the last few years and GC-MS respectively LC-MS are to be considered the most selective available methods.

In recent years few laboratories have gained experience with home made element-specific detectors. These mainly consist of plasma-emission-spectrometer coupled to capillary gas chromatographic systems.[1,2,3,4] The eluate coming from the GC is injected in a high-frequency or microwave induced helium plasma. The organic compounds already separated by GC are atomized at temperatures of a few thousands degrees and radiation is emitted by the excited atoms. Every single element of the separated compound can be detected by an appropriate spectrometer.

As most important advantages of this so called PED can be pointed out:

1. All elements appearing in a GC peak can be measured selectively down to the pg-region. Therefore overlapping substances may be detected free of interferences, if the compounds contain different hetero-elements.
2. The calibration is easier compared to other detector systems because only one single standard is needed for the calibration of a multitude of compounds of varying composition.
3. With a suitable setup of the PED all elements of the separated compound can be measured simultaneously. In this way the molecular formula can be calculated.
4. Deuterium has a separate line. This means that deuterinated compounds can be distinguished from not deuterinated compounds.

In 1989 several PED systems will be commercially available. One was developed by Camman *et al.*[3] and uses a MIP (Microwave Induced Plasma) as plasma light source, as other prototypes used in many laboratories do. Another PED developed by Hewlett Packard is equipped with a MIP as excitation source and a photodiode-array spectrometer. A third commercial available PED system, developed by our group in collaboration with Anton Paar Company (Graz, Austria), uses a completely new plasma source, the so called SCP (Stabilized Capacitative Plasma). One of the major advantages of the SCP compared to the MIP is that even a relatively large quantity of solvent (up to a few mg!) never lead to an extinction of the plasma. Both excitation sources use helium as plasma gas.

## PLASMA EMISSION DETECTOR

Figure 1 shows schematically the components of our GC-PED instrument. The central unit of the system is a new plasma light source developed during the last 4 years by our group.[10] Figure 2 depicts the layout of the Stabilized Capacitative Plasma (SCP). In contrast to the MIP normally used for element specific detectors, the SCP works with radiofrequency at 27.12 MHz. The RF energy up to 200 W is capacitively coupled to the plasma. The main advantage consists in the higher

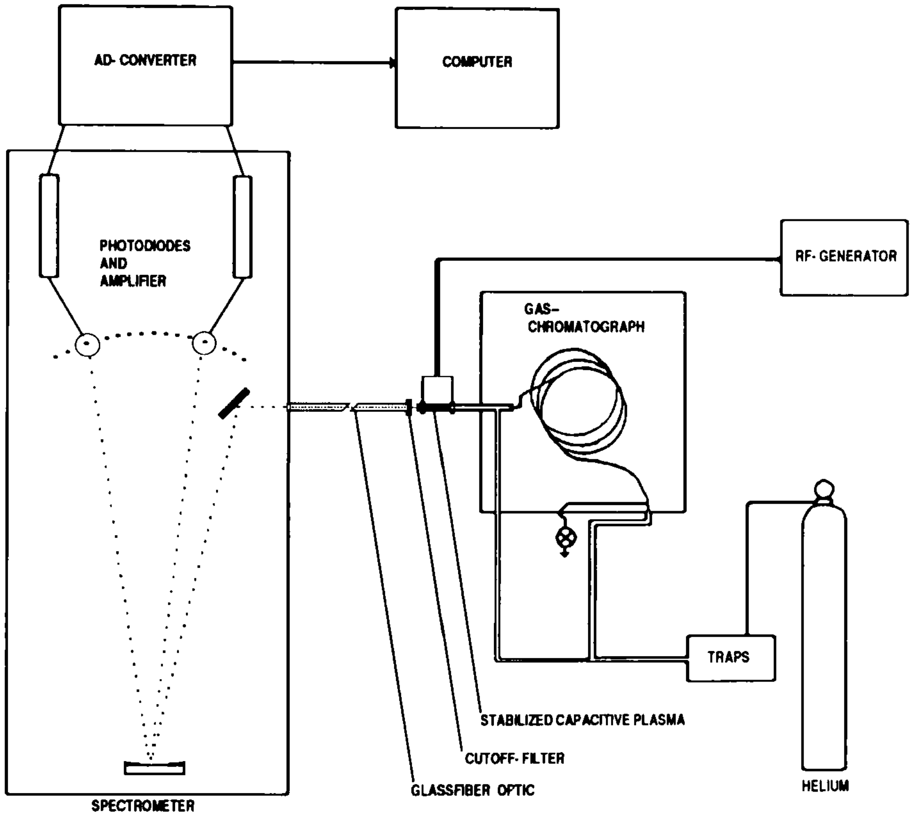

**Figure 1** Scheme of GC-PED system.

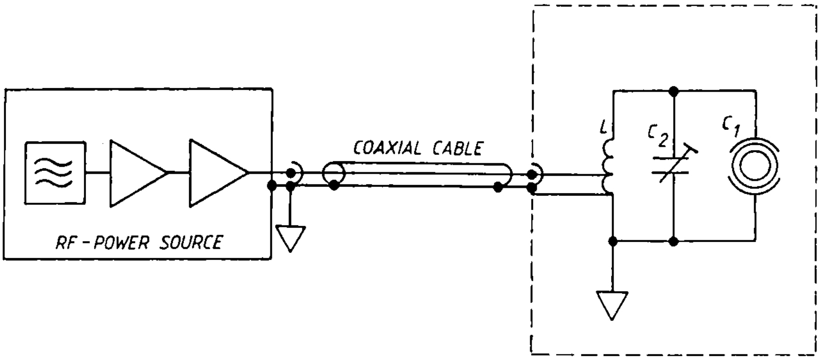

**Figure 2** Stabilized Capacitive Plasma (SCP), principles of operation. $L$ inductance, $C_1$ discharge, $C_2$ variable capacitor.

long-term stability of the plasma and the minor matrix interferences. Helium is chosen as plasma gas because of its high excitation energy for the halogens, but in principle every gas will work for the SCP even at atmospheric pressure. This fact is important for the application of this detector in supercritical fluid chromatography. The plasma tube consists of quartz, boron nitride or corundum, and is mounted directly to the end of the capillary of the GC.

The emitted light from the plasma is transferred to a spectrometer by an optical interface consisting of a cut-off filter and a glass-fiber optic with cross-section transformation in order to provide maximum recovery of light.

The spectrometer consists of a polychromator with channels for the non-metal elements in the region between 650 and 1000 nm. Table 1 shows the employed emission lines. Instead of photomultipliers, photodiodes were employed, giving a better signal to noise ratio in this spectral region. The use of double-diodes with matching double secondary slits makes the simultaneous determination of the element line and the corresponding background possible. Eight elements (H, C, N, O, S, F, Cl, Br) can be simultaneously determined with this polychromator at the moment. Deuterium is measured with a separate monochromator. The data of all element and background channels can be stored and processed on an IBM-AT computer.

## INSTRUMENTATION AND APPARATUS

Plasma emissions detector as described before; gaschromatograph Hewlett Packard 5890; capillary column 30 m, DB-1 (100% methyl silicon) John & Wiley, fused-silica, 0.3 mm inner diameter, 0.25 $\mu$m layer.

## RESULTS AND DISCUSSION

The following data and chromatographic separations may show the usefulness and efficiency of a plasma emission detector.

In a measurement the spectral region used for the elements detected is very important. Non-metals (C, S, Halogens etc.) show emission lines both in the short wave range (200 to 550 nm) and in the long wave range (650 to 1000 nm).

Figure 3 shows a spectrum in the region of 450 to 900 nm. The plasma

**Table 1** Emission lines used with the SCP.

| | |
|---|---|
| D | 656.1 nm |
| H | 656.3 nm |
| F | 685.6 nm |
| He | 706.5 nm |
| O | 777.2 nm |
| Cl | 837.6 nm |
| N | 868.0 nm |
| Br | 882.5 nm |
| S | 921.3 nm |
| C | 940.6 nm |

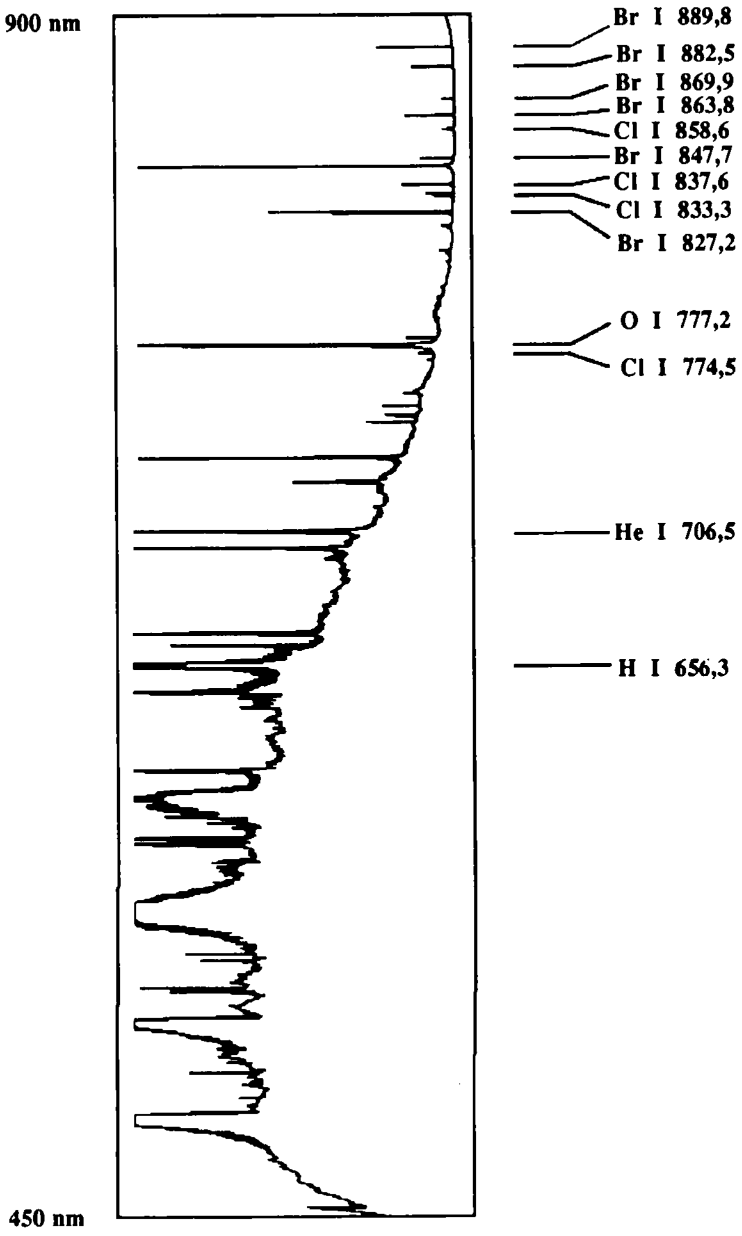

**Figure 3** Spectrum of sample-loaded plasma. Plasma: Stabilized capacitive plasma; 800 ml/min helium + 3 ml/min oxygen + 0.80 μg/sec $C_6H_5Cl$ + 0.37 μg/sec $C_2H_4Br_2$ + 1.16 μg/sec $C_6H_5F$; Spectrometer: Cerny Turner monochromator, 455 nm cutoff filter, SBW 0.14 nm.

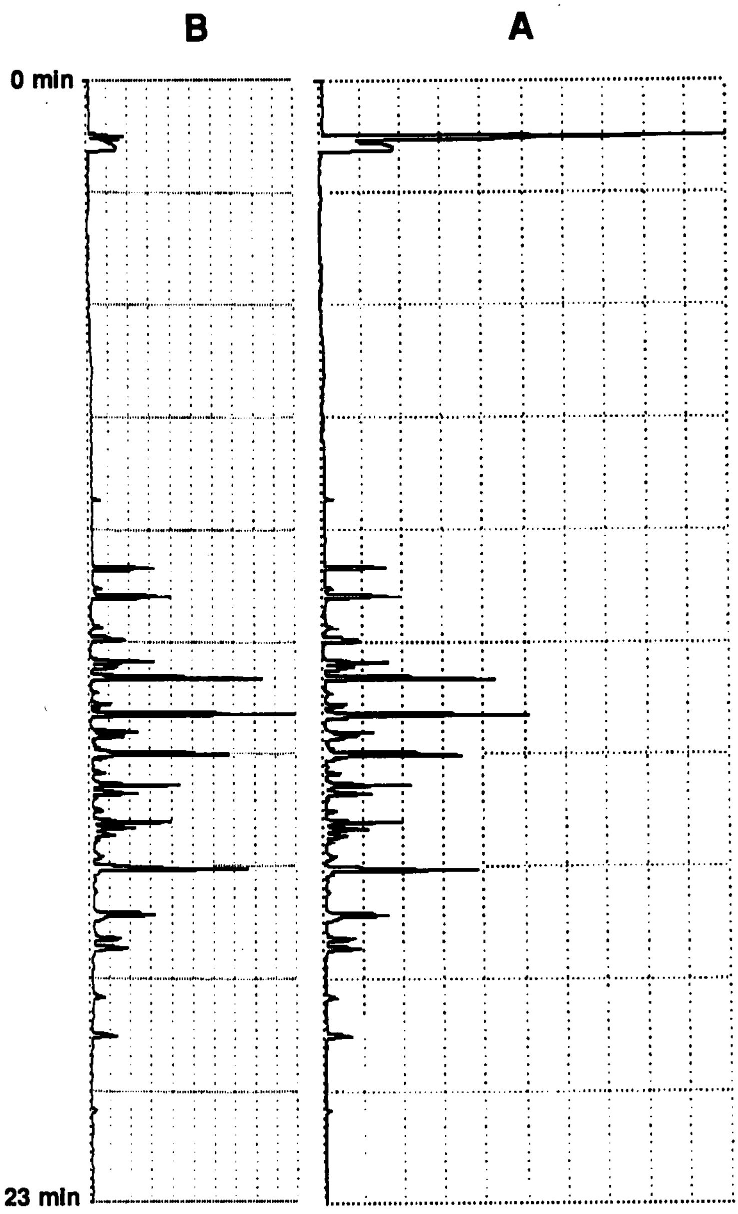

**Figure 4** Comparison of chromatograms (A) without, and (B) with background correction. Sample: PCB-mixture Arlochlor 1260®, sum of all PCB's 1 μg/μl (60% Cl); GC-parameters: Injector temperature 250 °C, detector temperature 280 °C, temperature program 1 min/100 °C, 20 min/190 °C, 4 min/260 °C; 70 kPa helium, sample volume 1 μl splitless.

**Table 2** Molecular formulas and element concentration of 6 pesticides

| | | *Element concentration (ng/µl)* | | | |
|---|---|---|---|---|---|
| | | *C* | *B* | *Cl* | *S* |
| 1. NALED$^{R}$ | $C_4H_7Br_2Cl_2O_4P$ | 30.2 | 100.2 | 44.6 | |
| 2. PHORATE$^{R}$ | $C_7H_{14}O_2PS_3$ | 77.3 | | | 88.3 |
| 3. DISYSTON$^{R}$ | $C_8H_{19}O_2PS_3$ | 70.3 | | | 70.4 |
| 4. RONNEL$^{R}$ | $C_8H_8Cl_3O_3PS$ | 60.0 | | 66.4 | 20.0 |
| 5. DURSBAN$^{R}$ | $C_9H_{11}Cl_3NO_3PS$ | 60.8 | | 59.9 | 18.0 |
| 6. ETHION$^{R}$ | $C_9H_{22}O_4P_2S_4$ | 61.7 | | | 73.2 |

background is drastically reduced starting from 650 nm, leading to a significant improvement of the signal to background ratio. In addition this region is practically free of molecular-bands.

The accuracy of an emission-spectrometric measurement among others depends on the consideration of the spectral background. In an ideal case this results in an absolute simultaneous recording of the background close to an emission line. We solve this problem by using a double-diode in combination with a double secondary slit with a distance of 50–100 µm.

Figure 4 shows chromatograms of a mixture of different PCB's detected through chlorine emission line with and without background correction. It clearly turn out that the non-specific peak of the solvent disappears nearly completely and only the peaks of the chlorinated compounds are visible. This means that even a great abundance of a substance does not have any influence on the measurement, even if it is not separated by chromatography from the chlorinated compound to be detected. Selectivity is about $10^4$ and the total mass of the PCB's separated was about 1 µg. Interferences are being studied in detail by our group.

Complex mixtures of substances often lead to complicated chromatograms and to overlapping peaks. The high selectivity of element specific detectors can overcome this problem, as long as the compounds to be separated contain different hetero-elements. Figure 5 shows a chromatogram of a mixture of 6 different pesticides. The respective tradenames with the molecular formulas are listed in Table 2 together with the concentrations of the single measured elements. As it turns out clearly the compounds can be distinguished through their different hetero-elements.

An example for the application to a real environmental sample is given in Figure 6. The chromatogram of a flyash extract was monitored at three different element lines. The upper trace shows the signal from the carbon channel. A similar chromatogram with many unresolved peaks one would obtain from a FID. The trace from the chlorine channel shows a typical pattern of polychlorinated biphenyls. On the sulfur channel there are only a few remaining peaks of sulfur containing polycyclic aromatic hydrocarbons.

The last point to be demonstrated is the possibility of a very simple calibration. We checked the concentration of commercial available standards for dioxin analysis. For the chromatographic measurement of these 8 compounds hexachlorocyclohexane and pentachlorophenol have been used as standards because of their

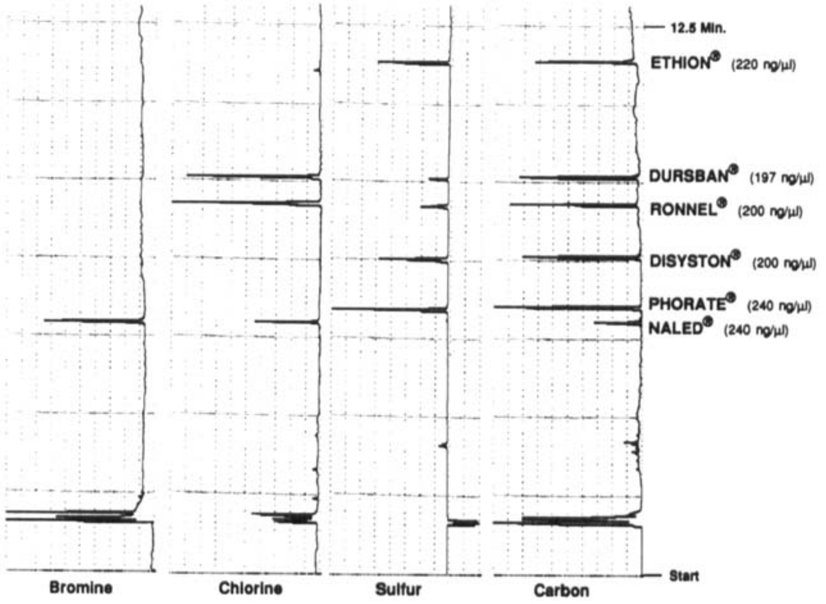

**Figure 5** Comparison of the detection at four different element channels (Cl, Br, S, C). Sample: Mixture of 6 different pesticides (Table 2); GC-parameters: Injector temperature 220 °C, detector temperature 280 °C, temperature program 1 min/130 °C, ramp 10 °C/min to 260 °C; 75 kPa helium, sample volume 1 µl splitless.

**Table 3** Calibration of commercial PCDD- and PCDF-standards

| *Compound* | *Concentration given (ng Cl/µl)* | *Concentration found (ng Cl/µl)* |
|---|---|---|
| 1. 1,2,3,4-TCDD | 11.0 | 10.9 |
| 2. 1,2,3,4,7-PCDD | 12.5 | 12.4 |
| 3. 1,2,3,4,7,8-Hexa CDD | 13.6 | 11.2 |
| 4. 1,2,3,4,6,7,8-Hepta CDD | 14.4 | 13.1 |
| 1. 2,3,7,8-TCFD | 11.5 | 11.3 |
| 2. 1,2,3,7,8-PCDF | 12.9 | 13.4 |
| 3. 1,2,3,4,7,8-Hexa CDF | 14.1 | 11.7 |
| 4. 1,2,3,4,6,7,8-Hepta CDF | 15.1 | 12.8 |

easy manipulation. Table 3 lists the compounds and the concentrations as indicated by the manufacturers against our results with the PED in the right column. As it turned out, the given values do not agree with the actually measured values. With a PED the use of these expensive and inexact commercial standards can be avoided. If these materials on the other hand are needed for other detector systems (ECD or MS) the PED allows a simple recalibration.

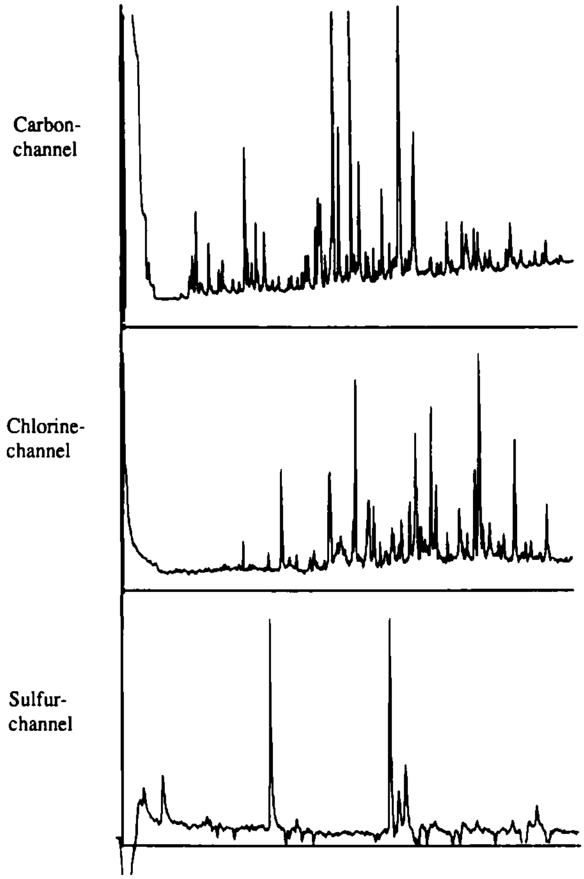

**Figure 6** Chromatogram of a flyash extract at different element channels (C, Cl, S). Sample preparation: 2.5 g flyash was extracted with toluene in a soxhlet-apparatus. The extract was evaporated to 2 ml. GC-parameters: Injector temperature 270 °C, detector temperature 300 °C, temperature program 1 min/180 °C, ramp 8 °C/min to 330 °C; 80 kPa helium, sample volume 1 $\mu$l splitless.

The Plasma Emission Detector with simultaneous multielement measurement constitutes a valuable supplement to a mass selective detector. Especially complex samples as encountered in environmental analysis are expected to be an important field of application in the future.

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