Element-selective trace detection of toxic species in environmental samples using chromatographic techniques and derivative diode laser absorption spectrometry

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Abstract. Very sensitive laser absorption techniques based on a double-beam scheme with logarithmic processing of the detector signals and wavelength modulation of laser diodes are presented. Detection limits equivalent to 10^{-7} absorption per square root of detection bandwidth are obtained if sufficient laser power is available and if the absorption is also subject to additional modulation. The analytical versatility of these techniques is demonstrated by quantitative analysis of very low concentrations of (i) Cr(VI) species in tap water and (ii) chlorinated poly-aromatics (chlorophenols) in plant extracts, both after chromatographic separation. The atomic absorption measurements were performed in an air–acetylene flame (Cr) and in a low-pressure microwave-induced plasma (chlorophenols).

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Although laser spectroscopy has proven its excellent analytical capability very early [1], tunable lasers are still exotic instruments in analytical laboratories. There were practical and economic reasons for the missing success of laser spectrochemical techniques in routine analysis. The most important tunable lasers, the dye lasers, were too complex and expensive, and they had to be operated by skilled persons. Furthermore, simultaneous multi-species analysis was impossible if there was only one tunable laser system available. This situation has changed in recent years when the first reliable and powerful semiconductor laser diodes became available. Semiconductor laser diodes of the AlGaAs and InGaAsP types combine the special spectroscopic properties of tunable cw lasers, such as narrow bandwidth and high spectral energy density, with technical and practical properties that are important for compact and routinely operated spectrochemical instruments of high sensitivity. The technical and practical properties are, for example, ease of operation, rapid wavelength tuning by diode current, room-temperature operation, low-amplitude noise, high stability, excellent efficiency, low price and small size. Although commercially available laser diodes still have a very limited spectral range (630–1600 nm) they can be used in analytical atomic spectrometry of many

elements if second-harmonic generation (SHG) in nonlinear crystals extends the wavelength range. In particular, the diode laser atomic absorption spectrometry (DLAAS) in analytical flames, graphite tube atomizer, and plasmas has proven its analytical power for trace analysis if wavelength modulation techniques are applied [2]. Very low detection limits have been obtained by DLAAS in comparison with the widely used conventional atomic absorption spectrometry (AAS) with hollow-cathode lamps [3].

Powerful techniques for element analysis are certainly very important in many application fields, in particular, in industrial analysis of gaseous, liquid, or solid samples. However, the knowledge of element concentrations is of much smaller relevance if environmental samples have to be analysed since the essential effect or the toxicity of elements depend on their binding form rather than on their total concentration. Therefore, analysis of environmental samples usually requires coupled techniques involving chromatographical separation steps before element-selective detection [4]. The scheme of the analytical procedure for speciation analysis is shown in Fig. 1. The atomic constituents of different molecular species in a sample are measured in a continuously operating atomizer, such as an analytical flame or a plasma. Fluorescence detection, mass spectrometry, absorption, or emission are applied after an appropiate chromatographic separation step. Plasmas which are popular in spectrochemistry are the inductively coupled plasma (ICP), the microwave-induced plasma (MIP), and the directly coupled plasma (DCP). Chromatographic techniques applied are, in particular, liquid chromatography (LC), gas chromatography (GC), electrophoresis, and supercritical fluid chromatography (SFC).

In the present paper, we will present two selected examples of environmental analysis which employ DLAAS and chromatographic separation, the measurement of chromium species in drinking water and of chlorophenols in plant extracts.

In the case of chromium, the oxidation states Cr(III) and Cr(VI) are of relevance, since the first species is an essential trace element for the human metabolism, whereas the latter is suspected to cause irreversible damage on organic tissue. The toxic properties of Cr(VI) species, predominantly occuring
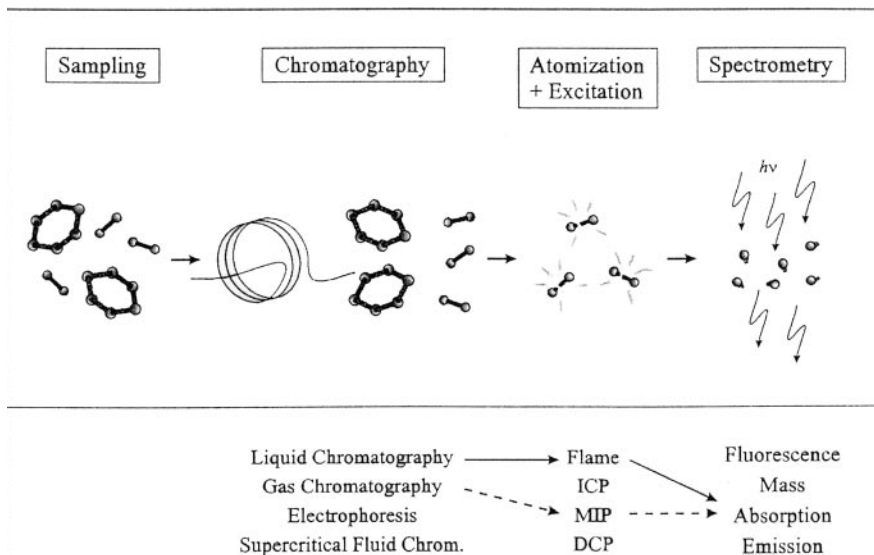
Fig. 1. Coupled techniques for species-selective analysis. The analytical procedure consists generally of sampling and sample preparation, chromatographical separation, atomization and, in some cases, excitation, and, finally, element-selective detection. In the lower box, solid arrows represent the coupled technique implemented for the speciation of chromium, whereas the procedure for the chlorophenol analysis is represented by dashed arrows

in forms of CrO_4^{2-} and CrO_7^{2-}, are due to the their capability of penetrating the cell velum of erythrocytes via anionic channels, which are on the other hand impermeable for the cationic Cr(III) compound complex [5]. It will be shown that DLAAS in analytical flames is capable of detecting Cr(VI) in tap water after LC even at concentration levels below 1 ng/ml regarded as harmless for human consumption.

The measurement of very low concentrations of chlorophenols in complex plant extracts is performed by element-selective DLAAS of metastable Cl atoms in a MIP after species separation by GC. The MIP is used as atomizer and excitation source for the Cl atoms. Production and trade of chlorophenols has been banned for many years in Germany and other countries because of their very high toxidity. However, they still appear in the environment, for example, near to incinerator plants for garbage if the burning temperatures are not high enough.

1 Experiment

Usually, absorption measurements are not considered to be very sensitive since the signal is a subtle variation of a large light flux. However, the employment of laser diodes enables us to measure these variations very efficiently. For example, the absorption of 10^{-8} causes a change of photon flux which exceeds the fluctuations determined by the shot noise if about 5 mW laser power in the red spectral range and a detection bandwidth of 1 Hz is applied. Theoretically, this value corresponds to the detection of about 10 atoms in an absorption path of $L = 10$ cm if the laser beam has a diameter of about 1 mm, a strong resonance line is used, and no optical saturation takes place. In practice, the signal is perturbed by additional noise contributions, such as intensity fluctuations of the laser source (laser excess noise) and optical interference effects (optical excess noise). Therefore, various modulation techniques have to be used to transfer the absorption signal into a high-frequency range where these noises can be eliminated and measurements at the shot noise limit can be performed. However, it has to be mentioned here that modulation techniques also reduce the absorption signal [6]. In a previous work we have investigated and critically analyzed appropriate modulation techniques for diverse noise terms and situations typical for measurements in analytical chemistry [7]. Table 1 summarizes the noise suppression and detection limits of various modulation techniques (wavelength and absorption modulation) with linear and logarithmic detection, respectively. The signal was linearly processed when only the sample beam was measured. Logarithmic amplification was employed when the reference beam was also measured. The laser wavelength was about 838 nm and the power 2 mW. A detailed discussion of the techniques and their noise suppression is given in [7].

In order to determine the detection limit that can be achieved applying a definite modulation $\omega(t) = \omega_0 + m \times \sin(\omega_{mod}t)$ we have to calculate the value of the modulated signal corresponding to the extinction of κL (κ: absorption coefficient). The amplitude of the (modulated) signal is $i\frac{\kappa L}{2}$,

Table 1. Noise suppression and detection limits in DLAAS obtained with 2 mW laser power, different modulation techniques, and linear (single-beam scheme) and logarithmic (double-beam scheme) signal processing

Modulation scheme	Detection	Noise suppression	Detection limit/ $AU/\sqrt{Hz}$
Wavelength	Linear	Laser excess noise	$\approx 10^{-5}$
Wavelength	$\ln \frac{I_S}{I_R}$	Laser excess noise*	$\approx 10^{-5}$
Wavelength + Absorption	Linear	Laser- and optical excess noise / RAM noise	$\approx 10^{-6}$
Wavelength + Absorption	$\ln \frac{I_S}{I_R}$	Laser- and optical excess noise / RAM noise*	$\approx 10^{-7}$

* Total suppression of laser excess noise

where i is the current of the photodetector in the absence of absorption.

Based on the relation between the modulation depth m and relevant noise terms, optimum S/N ratios in WM-DLAAS are generally obtained at second-harmonic detection [6], though the peak signal is slightly reduced in comparison with direct absorption and amounts, in the case of a Lorentzian line shape, to $0.35i\frac{\kappa L}{2}$[1]. This means that an absorption of $0.18\kappa L$ can be distinguished with high significance from noise.

Moreover, taking into account the internationally accepted 3σ criterion for detection limits (σ: standard deviation of the noise Δi_{noise}), the smallest detectable absorption is

$$A_{min} = \frac{3}{0.18}\frac{\Delta i_{noise}}{i} \approx 17\frac{\Delta i_{noise}}{i} \qquad (1)$$

for the considered Lorentzian line.

On the other hand, the shot noise is $\Delta i_{shot} = \sqrt{2ei\Delta f}$. Therefore, the detectable absorption – given by (1) – is limited to

$$A_{min} \approx 17\frac{\Delta i_{shot}}{i} \approx 25\sqrt{\frac{e\Delta f}{i}}, \qquad (2)$$

where e denotes the charge of the electron and Δf the detection bandwidth.

This means, for example, that a photocurrent of 3 mA corresponds to a smallest detecable absorption of $A_{min} = 1.7 \times 10^{-7}$ within a bandwidth of 1 Hz, which is a typical situation for measurements with laser diodes. On the other hand, A_{min} amounts to 2.5×10^{-5} if radiation powers of about

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[1] $0.44i\frac{\kappa L}{2}$ for a Gaussian line [6]

1.5 µW (0.15 µA photocurrent) are applied. The latter absorption limit is typical for the chromium measurements reported in the present paper.

2 Chromium speciation

Recently we have investigated the capability of DLAAS employing analytical flames in combination with high-pressure liquid chromatography (HPLC) and a high-pressure nebulization system for the Cr(III)/Cr(VI) speciation analysis [8]. The power of the frequency-doubled radiation was only 70 nW since we used a $LiIO_3$ as nonlinear medium for 50 mW fundamental radiation from a laser diode. Although the detection limit was already very low (about 1 ng/ml), it was too high to detect Cr(VI) in ordinary drinking water. In the present work, a SHG power of about 3 µW was generated in a more efficient crystal ($KNbO_3$). The increase of radiation power improved the detection limit significantly and allowed us to detect Cr(VI) in tap water far below the level which is considered as toxic [5].

Figure 2 shows the basic experimental arrangement for the quantitative speciation analysis by DLAAS. For chromium, the chromatographical separation is performed by HPLC. The atomizer is a flame. An AlGaAs-type laser diode (SDL-5410, wavelength at room temperature: 853 nm, maximum output power: 50 mW) driven by a commercial laser diode controller (LDC 400 by Profile) was used. The wavelength of the laser diode was modulated sinusoidal using a commercial function generator (Wavetec FG 5000) at a frequency of 7.5 kHz. As already mentioned above, the collimated laser radiation was frequency doubled in a $KNbO_3$ crystal which was temperature tuned for phase matching. The atomizer was a commercial air–acetylene flame (Varian). The Cr absorption ($3d^5\,4s\,^7S_3 \rightarrow 3d^5\,4p\,^7P_3$ transition

Fig. 2. Experimental arrangement. The *dashed parts* of the figure represent modifications of the arrangement if the absorption is modulated

at 427.48 nm) was measured by a low-noise silicon photodiode applying phase-sensitive amplification at the second harmonic of the wavelength modulation frequency. Moreover, we applied a double-beam detection scheme with logarithmic subtraction similar to the arrangement described in [7] in order to compensate the background component at the second harmonic of the diode laser modulation frequency. This component arises by SHG in the nonlinear crystal, where fluctuations cause additional noise. The 2f signal of the lock-in amplifier (Stanford Research Systems SR-830) was fed into a personal computer via an analog–digital PC board with a sampling rate of 3 Hz.

A commercial HPLC system (Knauer) with a Eurosphere Rp C_{18} chromatographic column (also from Knauer) was used. The chromatographic separation required a special preparation procedure, consisting of the admixture of acetic acid to reach a definite pH value and tetrabutylammonium acetate for the ion-pairing process. Sample volumes of 1 ml were introduced into the HPLC system. A detailed description of the full procedure is given in [9].

Figure 3 shows a chromatogram of a tap water sample and of a blank (dashed curve). The Cr(VI) peak corresponds to a concentration of about 0.3 ng/ml. The detection limit was determined to be 0.1 ng/ml which corresponds to about 1.4×10^{-4} absorption (bandwidth: 0.5 Hz). The shot noise increased by a factor of $\sqrt{2}$ because of the double-beam scheme. Note, the absorption is very near to the theoretical detection limit given at the end of Sect. 1 if the factor of $\sqrt{2}$ is taken into account. The blank signal was measured with samples of bidistilled water with acetic acid and tetrabutylammonium acetate. The Cr(VI) peak is enhanced by a factor of 5 to 6 in comparison with the Cr(III) signal which appears much broader. This is due to the applied chromatographic procedure which favors the detection of Cr(VI).

It has to be stressed that similar detection limits in chromium speciation can only be expected if inductively coupled plasma mass Spectrometry (ICP-MS) is used in combination with HPLC [10]. However, ICP-MS is a bulky and expensive technique that is certainly much more difficult to use for on-line control during the recycling process of water than the simple and compact flame-DLAAS technique.
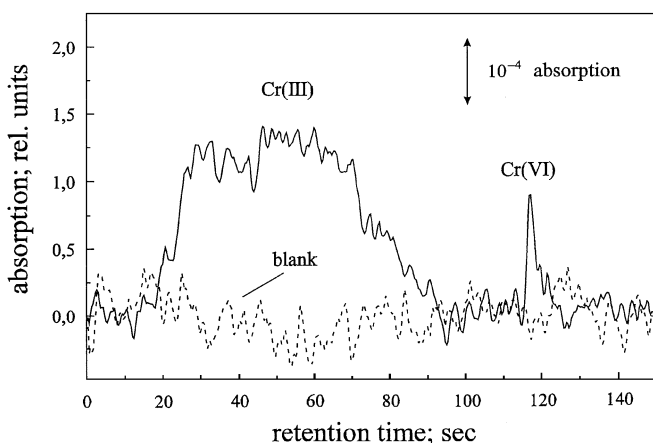
Fig. 3. Cr(III)/Cr(VI) speciation in tap water by DLAAS in an analytical flame. Cr is probed by the 427.48 nm line. The blank signal of bidistilled water is shown as dashed trace for comparison

3 Chlorophenol analysis

The modifications in the basic arrangement for the chlorine-selective detection of the volatile chlorophenols are shown by dashed lines and boxes in Fig. 2. The species were separated by means of a gas chromatograph (Shimadzu GC-14A with a fused silica column FS-SE-54-CB-1; column length: 50 m; inner diameter of column: 0.32 mm) with helium as carrier gas. The outlet gas flow of the column was directed through a quartz capillary (diameter 2 mm) where a MIP was sustained. The MIP was operated in a Beenakker-type resonator [11] at a pressure of about 20 mbar. The radiation of the laser diode was directed through the plasma on a silicon photodiode. The laser diode was tuned to the chlorine absorption line at 837.60 nm (3p 4s $^4P_{5/2} \rightarrow$ 3p 4p $^4D_{7/2}$) which probed the density of metastable Cl atoms in the plasma. The wavelength of the laser diode was modulated with a frequency of $f_{laser} = 11.5$ kHz. Additionally, the plasma was switched on and off with a frequency of $f_{plasma} = 5$ kHz. The signal was detected at the mixed frequency $f = 2 f_{laser} - f_{plasma} = 18$ kHz. This double modulation improved the S/N ratio significantly (see, for example, [7, 12]).

Chlorine-selective chromatograms of a standard sample and of a plant extract in n-hexane are shown in Fig. 4. Whereas the standard sample contains different types of chlorophenols, only trichlorophenol (TCP: $C_6H_4Cl_3O$) could be detected in the plant sample. The sample volumes were 1 μl. For the contaminated plant extracts, a detection limit of 30 ng/ml was found [13].

The advantage of element-selective detection by DLAAS can be seen if Fig. 4 is compared with Fig. 5, which diplays a chromatogram of a similar plant extract as recorded by DLAAS in a MIP, however, measured with an electron capture detector (ECD) [5]. The ECD is a non-specific detector which exhibits different sensitivities for different molecular species, commonly used for chlorophenol measurements. The ECD chromatogram of the plant extract shows many unknown components that do not contain Cl atoms. Furthermore, it has a sloping background because of overlapping components. Therefore, it is very hard to discriminate a small TCP signal from other components and, if one has located the chlorophenol, to give the exact magnitude of the signal. The DLAAS-detector chromatogram shows only Cl-containing components, in our case, only a TCP signal. Furthermore, there is the possibility of calibration by the addition of internal standards containing Cl or other elements because the element-selective signals reflect the stoichiometric ratios of the elements in the species [12, 14]. Element-selective detection in GC has been demonstrated not only for Cl but also for Br [12], C, and H [14].

It is not surprising that interlaboratory comparison studies of TCP in plants failed badly because the ECD was applied in all measurements. The TCP concentration found by different laboratories with ECD varied by about three orders of magnitude because of the strong interferences of the TCP signal with other matrix components.

There is another element selective detector used in GC, the atomic emission detector (AED). AEDs are based on atomic emission spectrometry of plasmas coupled to the gas chromatograph [15]. In principle, AEDs could also be used for the measurements of chlorophenols. However, the detec-
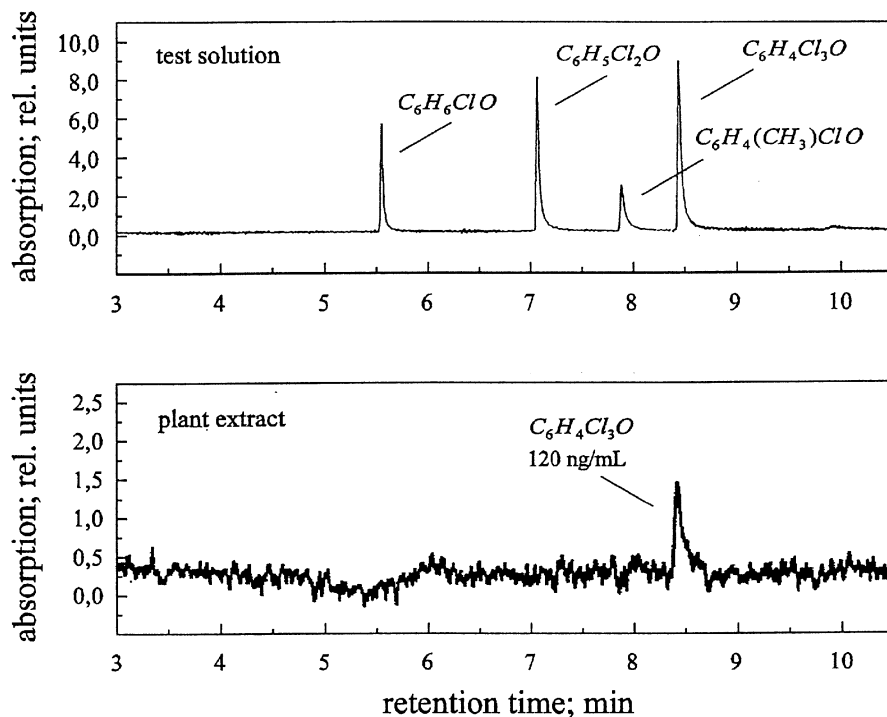
Fig. 4. Chlorine-selective chromatogram of a chlorophenol test solution (*upper curve*) and of a TCP-contaminated plant extract measured by GC-DLAAS of the Cl 837.60 nm line

tion limits of AESs are one to two orders of magnitude higher in comparison with DLAAS detectors [12].

4 Conclusions

Laser diodes are certainly key components for the transfer of powerful spectroscopy techniques from the research labora-tory to the fields of routine application. First commercial in-struments for element analysis based on DLAAS are already available. These instruments are still designed for applica-tion in routine laboratories. However, the present paper also shows that diode laser spectrometry can be a very powerful tool in environmental analysis where it has to be coupled with chromatography. Such devices are relatively simple and in-expensive, and can be engineered in such a robust form that they can be operated outside laboratories, for example, for environmental on-line control.

Fig. 5. Non-selective chromatogram of a TCP-contaminated plant extract using an electron capture detector

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