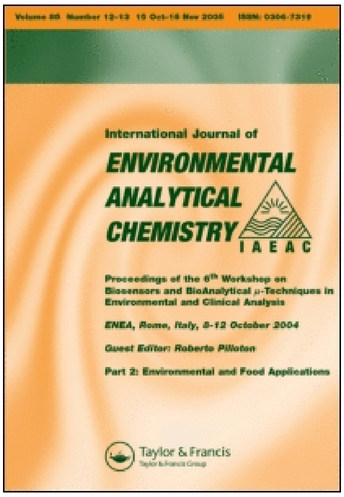

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Hirschberger, R. and D'orazio, M.(1992) 'Analysis of Automobile Exhaust Gases by a Raman Polychromator System', International Journal of Environmental Analytical Chemistry, 48: 2, 115 — 126
To link to this Article: DOI: 10.1080/03067319208027045
URL: http://dx.doi.org/10.1080/03067319208027045

Intern. J. Environ. Anal. Chem., Vol. 48, pp. 115–126
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ANALYSIS OF AUTOMOBILE EXHAUST GASES BY A RAMAN POLYCHROMATOR SYSTEM

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(Received, 13 August 1991; in final form 12 November 1991)

Automobile exhaust gases were analyzed by Raman spectroscopy using stationary and dynamic sampling of the gas. The Raman polychromator was designed especially for large optical throughput. The polychromator is based on a specifically corrected concave grating and F/0.7 optics at the entrance and the exit of the system. At measuring times in the order of 1 s, it was possible to correlate the carbon oxides, oxygen and hydrogen to nitrogen as standard. The detection of various hydrocarbons occurred at measuring times of several minutes. The contribution includes also a discussion of the nitrogen oxide problem.

KEY WORDS: Linear Raman spectroscopy, multichannel detection, automobile exhaust gases.

INTRODUCTION

For an employment of linear Raman spectroscopy as a routine method for the analysis of industrial waste gases, two criteria will be of special importance.

First, in contrast to infrared spectroscopy, Raman spectroscopy makes it possible to determine also homonuclear molecules such as O_2, H_2, N_2, where N_2 of the air may serve as a nearly ideal external standard for quantitative analysis. Furthermore, due to high symmetry or multiple bonds, molecules such as CH_4, C_2H_2, C_2H_4 provide prominent analysis bands in the Raman spectrum, and all the compounds cited play a dominant role, e.g. in combustional processes, or processes involving catalytic activities.

Second, for many years a Raman spectroscopic analysis of gases was difficult, since for gases the Raman signals are about three orders of magnitude lower than for condensed media, due to their low density and lack of an internal field[1]. However, nowadays, this drawback can be compensated by, amongst other reasons, the use of a powerful laser as light source. When it is possible to remove dust particles or aerosols from the sample, the false light will be very small which allows the employment of technically simple but very sensitive Raman spectrometers. Recently, special types of holographically formed concave gratings are available which makes it possible to design systems with very large optical throughput and which, in addition, are very suitable for adaption to multichannel detectors.

The statements cited should hold especially for an analysis of automobile exhaust gases. At present, according to the US-Test, Europa-Test or Japan-Test[2] the exhaust gases are sampled in containers, and subsequently the specified components are analyzed by various spectroscopic and non–spectroscopic techniques. The sum of hydrocarbons is determined by flame ionization detection, CO and CO_2 by non–dispersive infrared spectroscopy, NO_x by chemoluminescence, and O_2 by magneto–pneumatic, voltametry or related methods. While these procedures allow a detection of the compounds at fairly low concentrations, they are not suitable for simultaneous control of the compounds at rapidly varying operation conditions of the motor. Therefore, attempts are made to replace this procedure by a more unified spectroscopic method. A few years ago, for example, a strategy study was published[3], resulting in proposals based on Fourier-Transform-infrared and IR–diode laser spectroscopy[4,5]. The contribution presented here is concerned with the advantages provided by Raman spectroscopy as an alternative method.

For the measurements described below, the sampling was performed stationary (closed gas cell) as well as dynamically (transfer line and flow–through cell). Unfortunately, both sampling procedures were inhibited by condensation of the water vapor of the exhaust gas which led to solvation of the nitrogen oxides in the condensed water. Therefore, the determination of nitrogen oxides could not be included in the measurements and the nitrogen oxide problem will be discussed separately. These problems should not arise for an in situ application of the method, where the focus of the laser can be placed immediately at the end of the exhaust pipe, with a filter for soot and aerosols as the only interface.

The following section gives a short discussion of the combustional process in an automobile motor.

THEORY

The combustional process

At an "air ratio" $\lambda \leq 1$ (λ is defined as the ratio of oxygen in a fuel-oxygen mixture to the amount of oxygen necessary for a complete combustion) the combustional products CO, CO_2, H_2O, and H_2 are correlated by a so-called "watergas equilibrium"

$$CO_2 + H_2 \leftrightarrows CO + H_2O,$$

with a temperature dependent equilibrium constant K[6]. At temperatures below 1700 K to 1800 K the equilibrium will freeze and the ratio of the concentrations of the components will remain nearly constant, depending solely on λ. For a constant $K = 3.8$ which is typical for an Otto-motor, Löhner and Müller[6] calculated the composition of an water-free exhaust gas at varying λ as given in Table 1. Theoretically, for $\lambda \geq 1$, CO and H_2 should vanish—leaving just CO_2 and excess O_2. In practice, there will be CO remaining (in low concentrations), and in addition, noncombusted hydrocarbons and nitrogen oxides, which are formed from O_2 and N_2 of the air. Unfortunately, this formation of nitrogen oxides is especially efficient

Table 1 Concentrations in percent of components of an exhaust gas for varying λ and an equilibrium constant K = 3.8[6]

λ	CO	CO_2	H_2
0.7	11.5	7.5	6
0.8	7.5	10	3
0.9	3.5	12	1

for $\lambda \geq 1$, so that the request for a λ larger than 1 for low levels of CO contradicts the request for a low-level of nitrogen oxides.

Catalytic activity

The problem of a proper choice of the λ-ratio will get even more critical, when the pollutants CO and NO shall be further reduced by a catalyst in the exhaust. This may be attained by reactions as the following[7]

$$2CO + O_2 \rightarrow 2CO_2$$

$$2CO + 2NO \rightarrow 2CO_2 + N_2.$$

It can be seen that an excess of O_2 may leave too little CO for a reduction of NO and a deficit of O_2 decreases the oxidation of CO. This means, an efficient reduction of these pollutants requires a nearly stoichiometrically mixed exhaust gas with a λ-ratio close to unity.

EXPERIMENTAL

Instrumentation

The instrument in use is described in detail elsewhere[8,9] It is equipped with extremely powerful optics (F/0.7) at the entrance and the exit of the polychromator. The polychromator contains a Type IV holographically formed concave grating with 2000 g mm^{-1} and $f = 1020$ mm (first order) from Jobin Yvon. This grating allows the omission of any additional collimator optics in the polychromator. The curved spectrum produced by the grating was flattened by a special field lens arrangement for the adaption to the flat entrance window of the multichannel detector. The detector was a 1205 D SIT ('OMAI') with 500 channels from PAR, which was cooled to about $-15°C$. The spectral range recorded simultaneously corresponded to about 700 cm^{-1}. The laser in use was a Spectra Physics Ar^+ model 170. All measurements were performed with the line at 488 nm ($\approx$5W).

Sampling procedure

For stationary measurements a flexible bag containing an evacuated sample cell was filled immediately at the exhaust. After a few minutes, when the soot and most of the aerosols had settled, the cell was opened and filled. The settling of soot simulated a fairly efficient filtering procedure.

For dynamic measurements an asbestos covered metallic plait probe was placed into the exhaust with the end of the probe about 50 cm inside the exhaust pipe. This probe was connected by a flexible pipe with a filter, membrane pump (24 l min^{-1}) and an open end Raman gas cell. All measurements were performed on a 1.1 l Otto-motor with 40 KW at 5700 rpm.

Quantitative analysis

All signals were related to the signal of N_2 of the air as standard, accounting for the spectral sensitivity of the apparatus which was determined according to D'Orazio and Schrader[10]. The Raman scattering cross sections σ of the compounds of interest were taken from the literature[11]. The width of the entrance slit was set approximately equal to the width of the geometrical picture of the laser focus at the entrance slit, and corresponded to about 7 cm^{-1}. This means the effective halfwidth of the signals was much larger than the physical halfwidth of the bands of the gaseous compounds, i.e. it was approximately the same for all signals. Therefore, the cross sections could be correlated directly to the peak heigth of the signals which facilitates the quantitative analysis considerably.

RESULTS

Stationary measurements

The spectra shown in Figures 1 and 2 are each composed out of five single spectra (corresponding single spectra are shown in Figures 3–6). The measuring time for each single spectrum was 1 sec in the case of Figure 1. It is appropriate to correlate the signals of CO (concentration 6.8%), CO_2 (4.2%), O_2 (4.3%), H_2 (3.8%), and N_2 (74.2%) to N_2 of the air as external standard. The concentration of CO is comparatively high since the exhaust gas was sampled after starting the cold motor with a 'choke' which decreased the supply of air.

At a measuring time of 10 s (Figure 2) small signals corresponding to hydrocarbons are recognizable. An appropriate determination of hydrocarbons afforded measuring times of several minutes as shown in Figures 3–5. The concentrations were 180 mg l^{-1} for CH_4,40 mg l^{-1} for C_2H_4, and 130 mg l^{-1} for C_2H_2.

Figure 6 shows part of the spectrum of a sample different from that corresponding to the preceding figures. In this case the exhaust gas contained an atypically large amount of soot and aerosols (which is responsible for the plasma lines in Figure 6). In this spectrum a band was recorded at exactly 1000 cm^{-1} which is typical for a mono- or meta-disubstituted benzene ring[12].

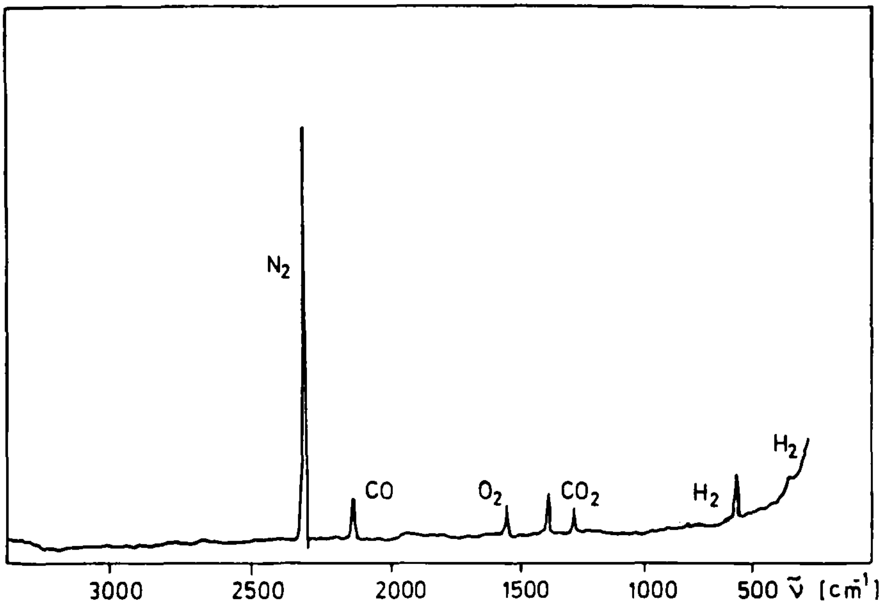

Figure 1 Raman spectrum of an automobile exhaust gas; measuring time 1 s.

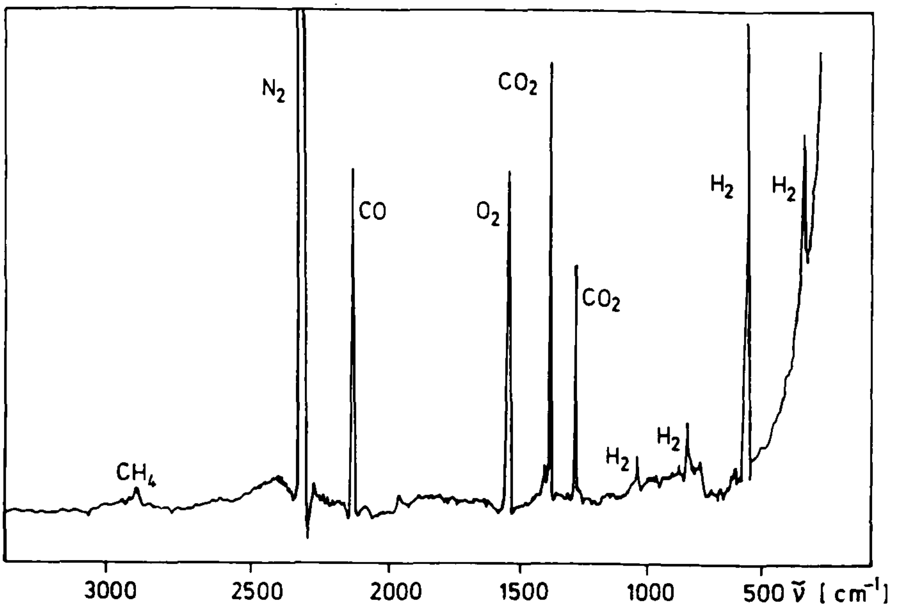

Figure 2 Raman spectrum of an automobile exhaust gas; measuring time 10 s.

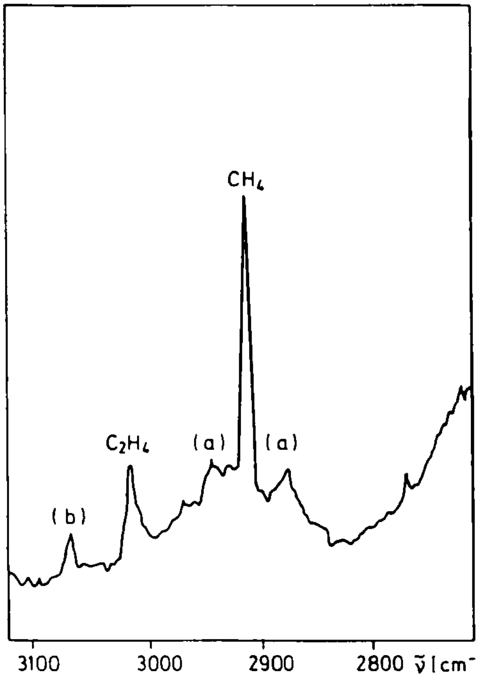

Figure 3 Raman signals from an automobile exhaust gas; (a) aliphatic, and (b) aromatic hydrocarbons; measuring time 10 min.

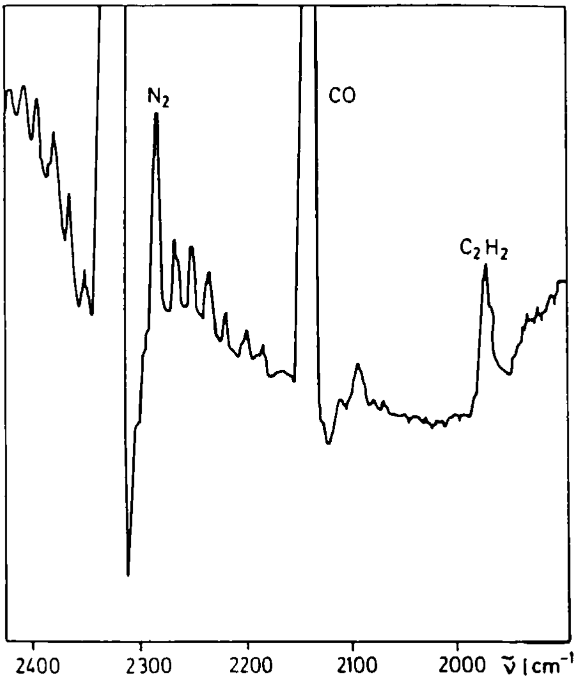

Figure 4 Raman signals from an automobile exhaust gas; measuring time 10 min.

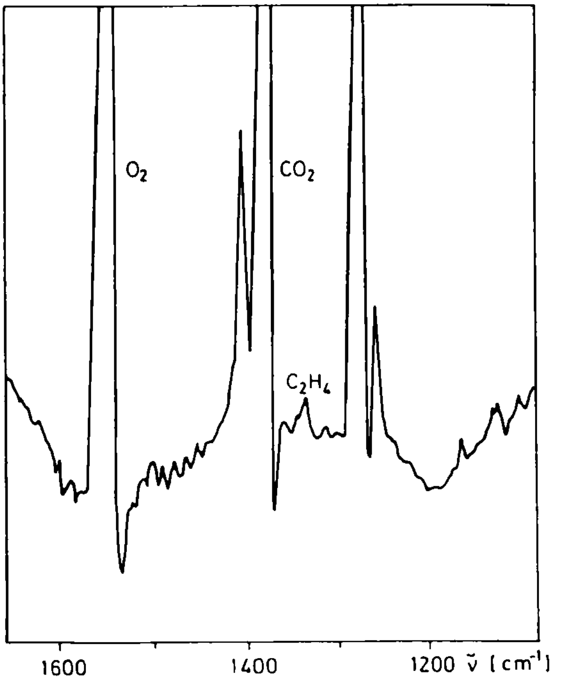

Figure 5 Raman signals from an automobile exhaust gas; measuring time 10 min.

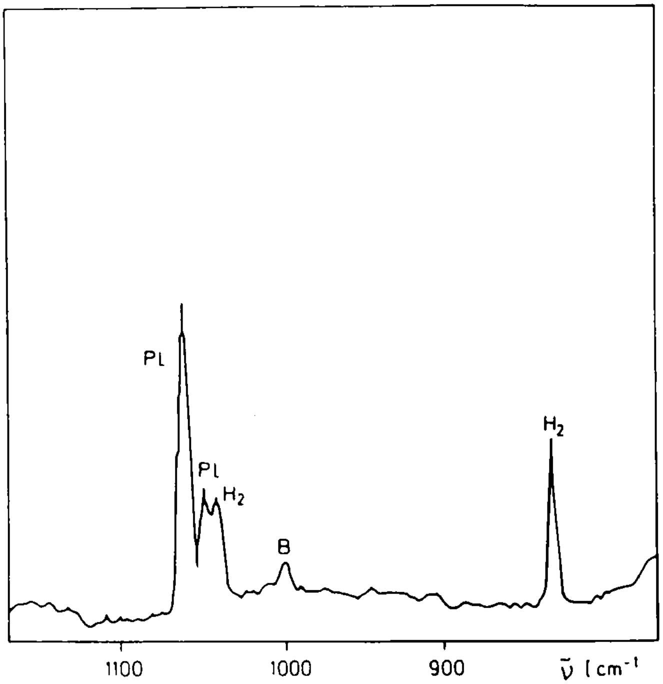

Figure 6 Raman signals from an automobile exhaust gas; B mono- or metadisubstituted benzene ring; PL plasma line; measuring time 30 s.

Dynamic measurements

These measurements were performed by connecting the exhaust by a transfer line immediately with the Raman spectrometer.

Figure 7 shows the concentrations of the components N_2, CO_2, CO, H_2, and O_2 in dependence of the speed of the motor which was heated by previously driving the car. Figure 8 shows the same components at cold motor with a choke reducing the air supply (see lower concentration of N_2 compared to Figure 7).

It was intended to demonstrate by these measurements the acute sensitivity of the

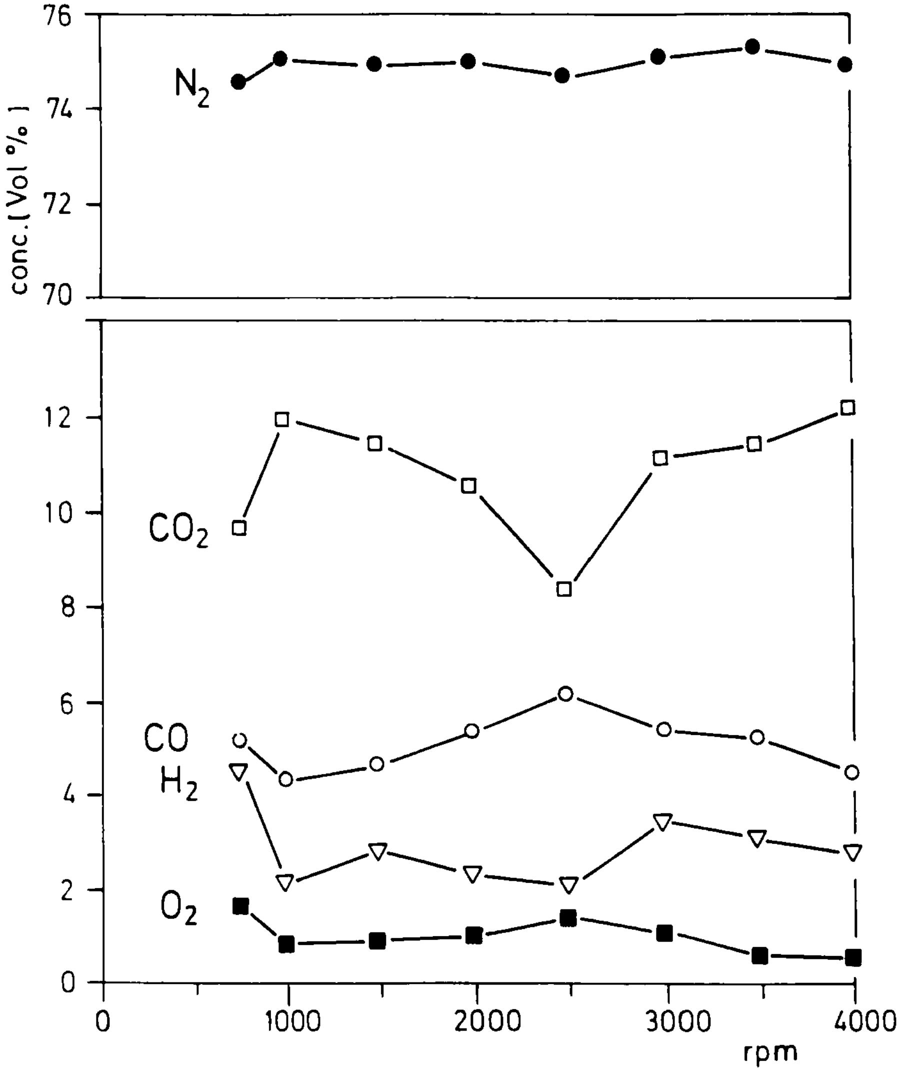

Figure 7 Concentrations dependence of automobile exhaust gas components on the speed of a hot motor.

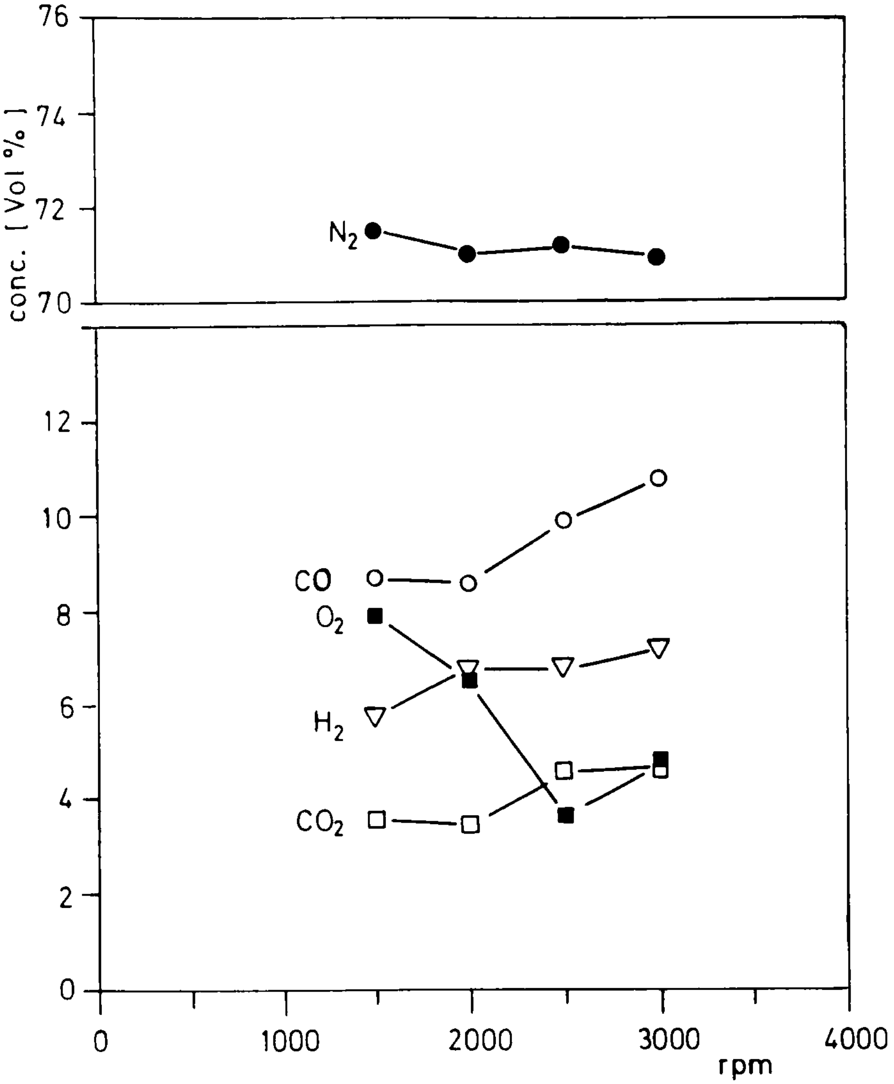

Figure 8 Concentrations dependence of automobile exhaust gas components on the speed of a cold motor with reduced air supply.

concentrations of the components cited to the operational conditions of the motor, and their suitability for monitoring especially the diatomic homonuclear compounds.

Nitrogen oxides

It was mentioned above that with the sampling procedures employed, the nitrogen oxides were largely removed from the exhaust gas by solvation in the condensed water—a problem which should not arise for an entire in situ analysis, with the laser focus immediately at the end of the exhaust pipe.

The species of nitrogen–oxides present in the exhaust gas depend critically on the temperature of the gas. In the motor the nitrogen–oxides should be represented nearly exclusively by NO. Below temperatures of 150°C, in contact with oxygen, NO will be increasingly converted into NO_2, resulting at normal temperatures in a well defined equilibrium between NO_2 and N_2O_4[13]. Therefore, the ratio of the concentration of the various nitrogen–oxides will depend entirely on the distance between the motor and the measuring point, i.e. on the degree of cooling of the gas after its emission from the motor.

For a determination of NO measuring times of several minutes would be necessary since the Raman scattering cross section of NO (1877 cm^{-1}) is relatively small ($\sigma(NO) = 0.4 \times \sigma(N_2)$)[11]. For measurements at comparatively cool exhaust gases, where the concentration of NO is very low it would be sufficient to determine the concentration of NO_2 and calculate the concentration of N_2O_4 according to the temperature of the exhaust gas. The scattering cross sections of NO_2 are resonance

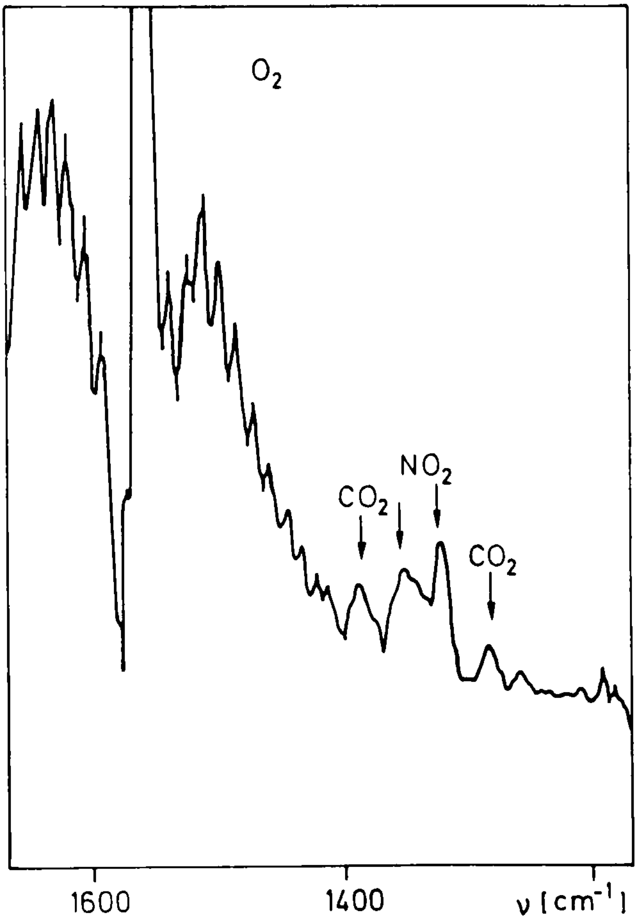

Figure 9 Raman signals of a synthetic NO_2/air mixture, conc. (NO_2) 45 mg l^{-1}; measuring time 30 s.

enhanced. Figure 9 shows part of the spectrum of a synthetic NO_2 air mixture, recorded with a measuring time of 30 s, and where the concentration of NO_2 was 45 mg l^{-1}.

DISCUSSION

The proposed technique is easy to handle for a routine analysis, and it is characteristic for conventional Raman spectroscopy that it allows, in general, a simple sampling technique even with critical samples. With the provision of an efficient filtering of soot and aerosols the laser focus can be placed either at the end of the exhaust pipe, or, with the use of windows, at places between the end of the exhaust pipe and the exit of the engine (there were also Raman spectroscopic investigations reported which were performed inside the engine[14,15]). Measurements at various distances from the exit of the engine may be useful since with the distance the temperature changes and this will influence the aggregate state of components (water) and the distribution between the species of a class of compounds (nitrogen oxides).

Criteria as technical feasibility will also play a role in the discussion on the choice between linear and nonlinear Raman techniques as, for example, "coherent anti-Stokes Raman spectroscopy" (CARS)[16]. Several CARS–investigations concerned with combustional processes have been performed. A report by Eckbreth *et al.*[17] dealing with jet engine exhaust shall be cited representatively among many others. Though there are very promising results, CARS yet reveals some drawbacks with respect to routine analysis. The technique is more complicated than linear Raman techniques. Nonlinear concentration dependency of the signals and concentration dependency of line profiles complicate the quantitative analysis. Furthermore, the costs for the equipment are comparatively higher.

For automobile exhaust gases the advantage of the accessibility of homonuclear diatomic compounds may be illustrated best by the problem that catalysts shall be employed. As denoted above, an efficient catalytic reduction of both NO and CO affords a nearly stoichiometrically premixed exhaust gas with a λ-value close to 1. Up to date this λ-value is controlled solely by monitoring O_2, and this monitoring is accompanied with various difficulties. Magnetopneumatic determination is disturbed by other paramagnetic components as nitrogen oxides, electrochemical determination requires a lead-free fuel to avoid poisoning of the platinum electrodes, and voltammetric determination cannot be performed directly in the hot exhaust gas[3]. With the Raman-spectroscopic method described it is not only possible to determine O_2-concentration simultaneously with the other components of the exhaust gas, but also to compute the λ-value theoretically from watergas reaction because of the possibility to determine at the same time of the H_2-concentration.

With the use of a powerful UV-laser it should be possible to enlarge the number of detectable compounds. Gaschromatographic investigations show that polycyclic aromatic hydrocarbons may be present in concentrations up to the order of 1 mg l^{-1} in the exhaust gas (chrysene $\approx$ 0.7 mg l^{-1}, fluranthene $\approx$ 1 mg l^{-1})[18]. At these concentrations these compounds should be detectable either by resonance Raman or by fluorescence. In the gaseous phase, compounds fluorescence has not only larger quantum efficiency than in the liquid but, in general, it reveals distinct vibrational structure and will, therefore, gain in specifity. A very convenient UV-laser system is provided by an excimer-laser driven dye laser equipped with a frequence doubling device. The special type of grating in use allows an easy change of the spectral range. Therefore, one can decide whether to record unperturbed Raman signals in the visible or fluorescence structures in the UV region.

CONCLUSION

A Raman-polychromator was used which is based on a holographically formed concave grating and an intensified multichannel detector. With this equipment it should be possible to employ the advantages of Raman spectroscopy especially for an analysis of gaseous systems with temporarily varying concentrations of the components, which is demonstrated by an investigation of automobile exhaust gases.

Acknowledgements

The authors thank R. Kuckuk for technical assistance and the Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen and the Bundesminister für Forschung und Technologie for financial support.

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