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Application of Laser Ionization Mass Spectrometry for On-line Monitoring of Volatiles in the Headspace of Food Products: Roasting and Brewing of Coffee

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Resonance-enhanced multi-photon ionization time-of-flight mass spectrometry (REMPI/TOFMS) has been applied to the detection of volatiles in the headspace of brewed coffee and in the coffee roasting process-gas. A frequency quadrupled Nd : YAG laser (266 nm) was used for REMPI ionization (REMPI@266nm) of the volatiles in an effusive molecular beam inside the ion source of a linear TOF mass spectrometer. A special sampling system provided a time correlated sampling. Under these circumstances REMPI@266nm is highly selective for ionization of phenolic compounds. Several phenolic compounds, such as the flavour-active 4-vinylguaiacol, can be detected in the headspace of coffee brew as well as in the roast off-gas with the application of this approach. Moreover, the nitrogen heterocyclic compounds, indole and caffeine, were detected in both cases.

During the roasting process the relative changes in concentration of some volatile components of coffee have been recorded by EMPI@266nm with a time resolution of 1 Hz. The different volatiles exhibit characteristic concentration profiles as a function of the roast time. These results demonstrate the applicability of REMPI-TOFMS for on-line monitoring of coffee processing technologies. Such an on-line monitoring technique is of particular interest for process-control purposes, e.g. quality-protection or feedback process control. For example, monitoring of off-gases from the coffee roast process or monitoring of certain unit operations during the instant-coffee manufacturing could be promising industrial applications.

Next to wheat, coffee represents the second most important food in world trade.[1] Taking the high value of coffee and its world production of 5.4×10^6 tons into account, the large commercial importance of coffee-processing is obvious. This is particularly true for the roast process, as the typical coffee flavour mostly arises during the roasting of the green coffee beans. Standard roast processes last 8–12 min at 180–240 °C. Compared to this, more progressive, faster processes take 2–3 min at 300 °C.[1] During the roast process, thousands of different chemical compounds are are produced by pyrolysis of the organic material of the green coffee beans. About 800[2,3] volatile compounds have been identified and many of them contribute to the coffee flavour.

The analysis of coffee volatiles is still a challenge for modern trace analysis. Usually, extensive and time-consuming enrichment, sample preparation and clean-up procedures (adsorptive trapping, steam distillation, fractionation, liquid chromatographic separations etc.) are necessary prior to an instrumental analysis by methods such as gas chromatography/mass spectrometry (GC/MS) or high-performance liquid chromatography (HPLC).[4] A lot of work has been done, using these highly sophisticated analytical techniques, to identify compounds that are decisive for the unique taste and flavour of coffee and, therefore, probably most of the major flavour-active substance classes are known.

Due to the fundamental importance of the roast process for the aroma and quality of the final coffee product, the coffee industry carries out extensive research activities in order to get a better insight into the formation of the roast products and the dependence of the final chemical composition on processing parameters. In particular, the development of on-line monitoring devices to assess time-concentration profiles of specific volatiles during coffee processing (roasting, decaffeination, instant coffee manufacturing) is of the utmost importance for fundamental studies on the generation of flavour-active compounds, their release kinetics and their degradation as well as for process control and optimization in industrial applications. However, due to the complexity of materials such as the roast gas, it is extremely difficult to achieve a fast, species-selective detection.

Only a multi-dimensional, highly selective and very sensitive analytical technique will permit a direct, species-selective on-line monitoring of coffee volatiles. Probably the best method for this challenge is the combination of resonance-enhanced multi-photon ionization and time-of-flight mass spectrometry (REMPI-TOFMS[5–9] or laser mass spectrometry) which presents a two-dimensional technique that couples selective ionization with mass-selective detection. Briefly, in REMPI-MS one intermediate state of the analyte molecule of interest is selectively excited by absorption of a laser photon (i.e. the wavelength of a wavelength-tunable laser is set to be in resonance with the appropriate UV transition). The excited molecules are subsequently ionized by absorption of an additional laser photon and then mass analyzed by the time-of-flight mass

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spectrometer. The selectivity of this technique is introduced by the resonance absorption of the first photon, i.e. by UV spectroscopy. As previously shown, this technique offers a selective detection of trace compounds in complex matrices; isomer-selective ionization is achievable if a supersonic jet inlet is used for sample gas cooling.[6,7,9] Even with a REMPI-TOFMS setup that uses a suitable fixed-wavelength laser and an effusive gas inlet (warm sample gas) it is possible to achieve a reasonable selectivity (e.g. operation at 266 nm, the fourth harmonic frequency of the Nd:YAG laser, for the detection of substituted benzenes.[8] This technique has already been successfully applied for time-resolved analysis of automotive exhaust gases.[8]

In this paper we investigate the possibility of a direct on-line monitoring of volatiles in coffee-process gases by REMPI-TOFMS.

EXPERIMENTAL CONCEPT AND SETUP

The REMPI-ionization technique is a compound-selective ionization method. This selectivity may be achieved by exploiting (i) specific UV absorption bands, (ii) differences in the ionization potentials (IP) or (iii) the different lifetimes of the intermediate excited molecular states of the compound to be analysed. High selectivity is needed, since, up to now, about 800 volatile compounds have been identified (mostly by GC/MS, the backbone analytical technique for the analysis of volatiles in food products) in roasted coffee.[3] These include hydrocarbons, alcohols, aldehydes and ketones, acids, esters, lactones, bases (mostly nitrogen heterocyclic compounds), sulfur compounds, acetals, phenols, furans, oxazoles and others.[3] We decided to start our investigation with a single laser wavelength, the easily available fourth harmonic of the Nd:YAG laser at 266 nm. Therefore, in a first step, we screened the listings of volatiles already identified in coffee[3,4] and tried to identify compounds that should be detectable by REMPI-TOFMS with an effusive gas inlet, using the 266 nm laser wavelength and that occur in concentrations of at least 0.1 ppm (ppm ~ mg/kg) in ground coffee.

The molecular properties required for two-photon REMPI detection at 266 nm (REMPI@266nm) are a non-vanishing photon absorption cross-section at 266 nm, intermediate-state lifetimes longer than *ca.* 100 ps and an IP below 9.32 eV (REMPI processes of higher order can be neglected with the chosen experimental setup). Taking these prerequisites into account, a sensitive REMPI@266nm detection is restricted mainly to substituted benzene derivatives, polycyclic aromatic compounds or conjugated, highly unsaturated compounds. The relatively abundant benzene-related nitrogen heterocycles (pyridines, pyrimidines, pyrazines, etc.) are suppressed in REMPI@266nm mass spectra since their IP values are larger than 9.32 eV.[6] The five-ring heterocyclic compounds (furans, oxazoles, pyrroles, thiazoles, etc.), which are also important are not accessible by REMPI@266nm, as their first UV transitions (S_1) are located below 266 nm (e.g. S_1 of furan is found at 230 nm.[10] A careful consideration of the available spectroscopic information and several INDOS/S-CI and AM1 calculations (for determination of UV transition energies and ionization potentials) led us to the conclusion that the phenolic compounds should be preferentially detectable by REMPI@266nm-TOFMS. Phenol derivatives are formed during the roast process by pyrolysis of chlorogenic and quinic acids (~7% of the dry basis of green coffee[2] and occur in concentrations of ~15–50 ppm (total phenolic concentration after reference 4) in roasted *Arabica* ground coffee. Consequently, we tried to detect these phenolic compounds by REMPI@266nm-TOFMS in the coffee-brew headspace, as well as in the process gas of a coffee-roast simulation.

The experiments were performed with a robust and compact laser mass spectrometer, consisting of a simple linear TOFMS with a special sample inlet system, designed for time resolved automotive exhaust gas measurements,[11] and an attached Nd:YAG laser. The used laser mass spectrometer was a prototype of a commercial system (TurboTOF™), manufactured by Bruker-Franzen GmbH (Germany) after Boesl *et al.*[8] (for details see Ref. 11). The output of the frequency-quadrupled Nd:YAG laser beam (266 nm and repetition rate of 50 Hz), with an average pulse power of 2.0 mJ, 4 ns pulse length and a beam diameter of *ca.* 4 mm was coupled into the ion source of the TOFMS without focusing. The laser light intersected the effusive molecular beam directly underneath the inlet capillary. Data acquisition was performed with a transient recorder and mass spectra were obtained by summation over 50 laser shots. With this setup, detection sensitivities better than 1 ppb have been achieved for toluene and *p*-xylene.[12] From the vibronic structure in the UV spectra of the phenol derivatives and the REMPI sensitivities of phenol measured by others, a REMPI@266nm sensitivity for the phenol derivatives of the same order of magnitude as for toluene can be assumed. The relatively poor mass resolution achieved with the linear TOFMS used can easily be increased by using a reflectron instrument.[13] During the measurements, we observed memory effects from the sampling system for some less volatile compounds such as caffeine. For a new TOFMS apparatus, under construction within our group (especially designed for on-line trace analysis of complex gas mixtures), an improved sampling system, based on a suitably heatable, deactivated fused-silica capillary is being developed.

For the detection of volatiles in the headspace of coffee brew, a cup-shaped glass with a Teflon™ top was used. For the headspace analysis of brewed coffee, one heaped spoon of standard pure *Arabica*-blend, roast and ground, coffee was placed in the glass. Subsequently, boiling water (50 mL) was poured onto the roast and ground coffee; the coffee grounds were left in the brew. The headspace over the brew was sampled via a heated steel pipe, which was directly connected with the TOFMS sampling unit. The simulation of the roast process was performed as follows. A steel cylinder was heated on a laboratory hotplate to approximately 200 °C. Then, the cylinder was filled with 20–30 green coffee beans and sealed with a preheated steel top, containing steel pipes for sampling and ventilation. The heated sampling pipe was directly connected with the sampling unit of the TOFMS.

RESULTS AND DISCUSSION

REMPI@266nm analysis of the headspace of coffee brew

A typical REMPI@266nm mass spectrum of the headspace over *Arabica* coffee is shown in Fig. 1. A reliable assignment of the mass spectum is possible, since more than 95% of the coffee volatiles can be excluded, as being unable to contribute to the spectrum due to the optical selectivity of the one-color REMPI@266nm process. Further, only very weak, if any, fragmentation occurs, under the chosen

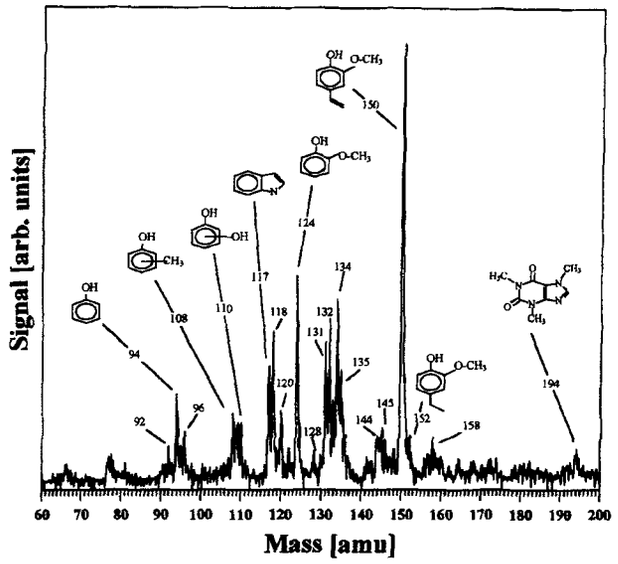

Figure 1. REMPI@266nm mass spectrum of the headspace over *Arabica* coffee brew with assigned mass numbers. The concentration of the major compounds (phenol, guaiacol, 4-vinylguaiacol) detected in the headspace, is estimated to be *ca.* 100 ppb. For further details, see text.

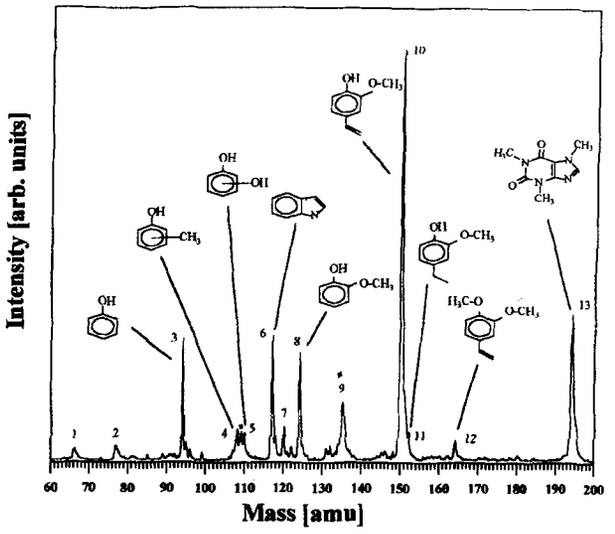

Figure 2. Typical REMPI@266nm mass spectrum assignment of the exhaust gas from a simulated roasting of green *Arabica* coffee beans at approximately 200 °C. The assignment of the mass spectral peaks is given in Table 1. The phenolic compounds dominate the spectrum even more as in the case of headspace analysis of brewed coffee. For further details, see text.

REMPI@266nm conditions (e.g. a weak methyl loss signal from methoxybenzenes is observable while the other phenolic compounds show fragmentation below 5% intensity as was verified with pure substances.[12] As mentioned above, a major contribution from phenolic compounds is expected in the REMPI@266nm-TOFMS mass spectra of coffee volatiles. Silwar *et al.*[4] list the most abundant phenol derivatives in coffee as 4-vinylguaiacol (M_r 150) and guaiacol (M_r 124), followed by phenol itself (M_r 94) and the cresols (M_r 108), in this order. Other relevant phenolic compounds are benzenediols (M_r 110), ethylphenols and dimethylphenols (M_r 122), vinylphenols (M_r 120), ethylguaiacols (M_r 152), and dimethoxystyrols (M_r 164). As shown in Fig. 1, several of these compounds could be assigned in the REMPI@266nm mass spectrum of the *Arabica* brew headspace.

The two most abundant peaks in the REMPI@266nm mass spectrum are due to the phenolic compounds that are most abundant in roasted and ground coffee, i.e. 4-vinylguaiacol and guaiacol. In order to verify our assignment, we repeated the brewing experiment, using a *Robusta* ground coffee under otherwise unchanged conditions. The concentration of 4-vinylguaiacol in brewed *Robusta* coffee is reported to be about a factor 7 higher than in *Arabica* coffees.[14] This is in accord with our observations, the relative and absolute intensity of the 4-vinylguaiacol peaks in the REMPI@266nm-TOFMS mass spectrum of the *Robusta* coffee brew headspace is largely increased with respect to the *Arabica* coffee headspace measurement (Fig. 1).[12] In an additional experiment, we performed a pyrolysis experiment with ferulic acid (ferulic acid is the precursor of 4-vinylguaiacol and occurs at about the 1% level in green *Arabica* coffee) under the conditions used for the coffee roasting experiments. The REMPI@266nm-TOFMS signals of 4-vinylguaiacol at *m/z* 150 (molecular ion) and the typical fragment at *m/z* 135 were very intense, leading to detector saturation effects.[12]

Beside the phenolic substances, two other compounds could be identified in the mass spectra shown in Figs 1 and 2, viz. indole and caffeine. Indole exhibits an extremely high REMPI@266nm efficiency and occurs in approximately the same concentrations as phenol.[4] Caffeine is very abundant in the roasted and ground coffee (% range) but is not very volatile. However, on the basis of the comparison with the REMPI@266nm mass spectrum of roasting off-gas (Fig. 2), the small peak at *m/z* 194 could reliably be assigned as caffeine. The peaks at *m/z* 135 and 109 are due to the weak fragmentation of methoxybenzene derivatives under REMPI@266nm (loss of the methyl groups of guaiacol and 4-vinylguaicol as verified in REMPI@266nm mass spectra of the pure compounds.[12] The peaks at *m/z* 118, 131, 132 and 134 are not yet assigned. The relatively poor signal-to-noise ratio in the mass spectrum is caused by the fairly low concentrations of the detected compounds in the headspace, which are probably in the 100 ppb range.

REMPI@266nm analysis of coffee roast exhausts

Figure 2 shows the mass spectrum of green-coffee-roasting exhausts. Just as with the experiments on the coffee brew, the mass spectrum is dominated by phenolic compounds because of the specific optical selectivity of REMPI@266nm. Due to the higher temperatures reached in the roasting experiments (over 200 °C) caffeine is visible with a relatively high intensity. The assignment of the peaks of the roast-exhaust gas REMPI@266nm mass spectrum is given in detail in Table 1.

Figure 3 shows the relative changes of the concentrations of guaiacol (*m/z* 124), indole (*m/z* 117), and 4-vinylguaiacol (*m/z* 150) during the roast process, as measured by REMPI@266nm. The on-line registration of the three compounds started some minutes after placing the green coffee beans in the hot steel cylinder. This time was required to mount the preheated steel top and connect the TOFMS sampling unit. Measurements were performed every second. As the laser repetition rate was 50 HZ, every single data point represents the numerically integrated area of the mass peak of the respective component, averaged over 50 laser shots. The periodic signal fluctuations visible on the time concentration profiles are caused by the temperature control of the hotplate.

Figure 3 shows that the guaiacol concentration increases continuously during the roast, whereas 4-vinylguaiacol reaches a maximum concentration and subsequently starts

Table 1. Listing of the assigned peaks in the REMPI-266nm mass spectrum of roast process off-gas shown in Fig. 2. The peak numbers (first column) correspond to the number in Figure 2. The typical concentration of the respective compound in *Arabica* coffee[4] is given in the last column.

Peak	Mass	Assignment	Typical concentration in *Aribica* coffee (ppm)
1	66	fragment from phenol	—
2	77	C_6H_5; fragment from phenolic derivatives	—
3	94	C_6H_6O; phenol	1.20–2.20
4	108	C_6H_6O; cresols	1.15–2.20
		C_6H_6O; methoxybenzene	
—	109	$C_6H_5O_2$; fragment from guaiacol ($M - CH_3$)	—
5	110	$C_6H_6O_2$; dihydroxybenzenes	
6	117	C_8H_7N; indole	0.30–0.80
7	120	2-phenylacetaldehyde	1.50–2.00
8	124	$C_7H_8O_2$; guaiacol	2.00–3.00
9	135	$C_8H_7O_2$; fragment from 4-vinylguaiacol ($M - CH_3$)	
10	150	$C_9H_{10}O_2$; 4-vinylguaiacol	8.00–20.00
11	152	$C_9H_{12}O_2$; 4-ethylguaiacol	0.80–1.50
12	164	$C_{10}H_{12}O_2$; 3,4-dimethoxystyrene	0.40–0.80
13	194	caffeine	2–4%

to decrease. The indole concentration in the roast gas decreases continuously after a steep initial increase. 4-Vinylguaiacol is known to be present in green coffee,[14] but the major part of the phenolic compounds is generated by degradation of organic acids as chlorogenic acid, caffeic acid, ferulic acid and quinic acid. For example, 4-vinylguaiacol is formed by decarboxilation of ferulic acid. It has been observed that, in dark-roasted coffee blends, the concentration of guaiacol is increased but that of 4-vinylguaiacol is decreased compared to light- or medium-roasted coffee.[16] This can be explained by the fragile thermal character of 4-vinylguaiacol; when higher roast temperatures/times are reached, the 4-vinylguaiacol concentration decreases due to its rapid decomposition, e.g. by cleavage of the ethylene group. Indole is already present in green coffee[15] and is probably not additionally formed during roasting.

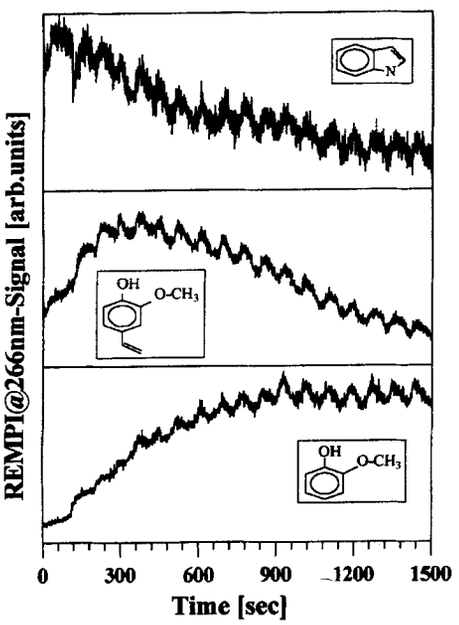

Figure 3. Time-concentration profiles of indole (*m/z* 117), 4-vinylguaiacol (*m/z* 150) and guaiacol (*m/z* 124) during the roasting process measured by REMPI@266nm. The ratio of the concentrations of two phenolic compounds could be used as a roast-degree indicator and is easily measured by REMPI@266nm-TOFMS. For further details, see text.

The roast profiles measured by REMPI@266nm-TOFMS are consistent with what is known from conventional analytical investigations. Thus, 4-vinylguaiacol and guaiacol are formed during roasting, but, due to the thermal instability of 4-vinylguaiacol, the latter compound decreases in concentration later on. The observed decrease of the indole concentration in the roast gas is probably due to the vaporization of the indole already present in green coffee. The different time-behavior of the volatile concentrations investigated, especially those of guaiacol and 4-vinylguaiacol, suggests the applicability of REMPI-TOFMS for on-line monitoring and control of the roast process.

CONCLUSION AND OUTLOOK

The results presented prove that, even with a relatively simple and therefore robust laser mass spectrometric setup (linear TOP, effusive molecular beam sample inlet and fixed laser wavelength) that is inexpensive and easy to handle, a successful application to on-line monitoring of volatiles of food products is possible.

It is important to question the validity of the peak assignments in the mass spectra presented. These assignments are verified by the following arguments:

(i) The optical selectivity of the REMPI@266nm technique excludes more than 95% of the known coffee compounds. This was verified in REMPI@266nm experiments on pure samples of compounds found in coffee volatiles. Extremely high REMPI@266nm efficiencies were obtained for phenol, guaiacol, 4-vinylguaiacol, indole and caffeine. For other compounds, e.g. pyrazine, furylthiol, 2,3-butadione, and furaniol, only very weak or even no REMPI@266nm signals could be detected from the headspace over the pure samples.

(ii) The fragment ions of 4-vinylguaiacol and guaiacol at

m/z 135 and 109 respectively (cleavage of methyl from the methoxy group, see asterisk in Fig. 2) exhibit the same relative intensities with respect to the molecular ion as observed in REMPI@266nm mass spectra of pure 4-binylguaiacol and guaiacol samples.

(iii) In accordance to the reported higher concentrations of phenolic compounds of *Robusta* coffee in comparison to *Arabica* coffee, the REMPI@266nm mass spectrum of the headspace of *Robusta* coffee brew exhibited significantly increased signals for 4-vinylguaiacol and guaiacol (obtained under the same condition as the *Arabica* coffee headspace mass spectrum shown in Fig. 1).

(iv) In a pyrolysis experiment we heated ferulic acid (content in arabic coffee: about 1%) and measured the pyrolysis off-gas with REMPI@266nm-TOFMS. The mass spectrum showed only 4-vinylguaiacol (very intense molecular ion peak at *m/z* 150, characteristic fragment ion at *m/z* 135.[12]

(v) The roast profiles obtained are consistent with the expectations drawn from investigations on the concentration of volatiles at different roast times performed with conventional techniques.[16]

In this work, only one laser wavelength was used. The application of other laser wavelengths for REMPI would allow the detection of other compounds, e.g. pyrazines, pyrroles, furans, oxazoles and carbonyl compounds. However, a careful investigation of the REMPI-spectroscopy of the aromatic and heteroaromatic and highly unsaturated compounds of interest is the prerequisite for a successful extension to on-line monitoring or other important coffee compounds with REMPI-TOFMS. By using two-color REMPI[7] and/or a supersonic jet inlet system (this allows a greatly increased ionization selectivity[6,17]) the field of application for the on-line REMPI-TOFMS method for registration of food product volatiles can be further extended. Many other applications in the field of food technology (e.g. control of the processing of cacao, tea or instant food), chemical technology (process control and emission monitoring[9]) or environmental analysis[18] are possible. Furthermore, an ultratrace analysis of volatile and semi-volatile coffee compounds can be performed by a gas chromatography/laser mass spectrometry (GC/REMPI-TOFMS) coupling.[18] The large clean up effort, necessary in conventional food flavour analysis, may be reduced considerably due to the high optical selectivity of REMPI, which then allows a relatively fast analysis of key flavour compounds, e.g. for quality control. The relative REMPI cross-sections for different compounds, e.g. for REMPI@266nm, necessary for the calibration and quantification of the REMPI-TOFMS on-line monitoring technique, can be obtained using the GC/REMPI-TOFMS technique.[18] An application of REMPI-TOFMS for industrial process-control purposes should be accompanied by conventional analytical studies (e.g. by GC/MS) in order to find important volatiles that can act as indicators for age, origin, quality or degree of roasting of coffee.

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