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Beer Digestions for Metal Determination by Atomic Spectrometry and Residual Organic Matter

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Abstract. Many standard and official sample digestion procedures for trace metal determination are carried out in open vessels on hot plates. A new procedure for the determination of trace metals by flame atomic absorption spectrometry or inductively coupled plasma-atomic emission spectrometry in beer samples was developed to be performed in closed reactors assisted by microwaves. The results are compared with the ones obtained by other procedures by means of the analysis of the variance. The differences between the procedures are attributed to residual organic matter. Voltammetry, absorption molecular spectrophotometry and high pressure liquid chromatography with a photodiode array detector are used to study the nature of these residues. Nitrobenzoic acids, phenolic acids and other organic compounds are often present after digestion. The results obtained are related to the precision in metal determination by atomic spectrometry. The need for elaboration of certified reference materials for trace metals in beer is suggested.

Key words: Beer; trace metal; microwave digestion; atomic spectrometry; residual organic matter.

Significant advances have recently been made in analytical instrumentation. However, sample decomposition techniques have not been developed to the same degree, in spite of the fact that this step contributes more to the total standard deviation of the analytical process than instrumental measurement. The advances in microwave-enhanced chemistry and its importance as a potential tool for overcoming the technological mismatch between sample preparation and instrumentation have recently been reported [1].

Beer has become an international drink, especially among young people. The health implications of trace elements are now well recognised, and trace element concentrations are subject to legislation [2].

A method proposed by The Royal Society of Chemistry [3] points out the necessity of destructing organic matter. This implies acid digestion with H_2SO_4 and H_2O_2 on a hot plate in an open beaker. This procedure is time-consuming and prone to loss and contamination. Nowadays, microwave heating systems in closed reactors have replaced many hot-plate procedures, because the digestion time and reagent consumption can be reduced and accuracy and reproducibility can be improved [4].

In this paper, a new sample preparation procedure for trace metal determination in beer based on the method proposed by the Royal Society of Chemistry has been developed. It implies the destruction of organic matter with the same reagents, but digestion is carried out in closed vessels and assisted by microwaves. The metals are determined by flame atomic absorption spectrometry due to its high selectivity,

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good precision and well-established methodology. Three procedures based on wet digestion are compared for the determination of Fe, Cu and Mn by atomic spectrometry (FAAS and ICP-AES). Fe and Cu were chosen because they play an important role as catalysts in the oxidation of organic compounds that are responsible for the stability and flavour of beers [5]. Mn concentration influences the brewing process [6]. In two cases closed reactors and microwaves are used, and in the third case, digestion is carried out on a hot plate. The analysis of variance was used as a tool for establishing the differences between the three procedures. Depending on the efficiency of the digestion procedure used, a significant amount of residual organic matter may remain in the digests, as described for biological samples [7–9] and for food samples [10]. In our case, residual carbon content (RCC) has been determined by ICP-AES in the beer digests. Voltammetry, molecular absorption spectrophotometry (MAS) and an HPLC-photodiode array detector were used to identify the nature of the residual organic matter and its relation to metal trace determinations.

Experimental

Instrumentation

A microwave oven (CEM MDS.2000) equipped with Teflon vessels (PFA, 120 mL, 220 psi) and a pressure regulator; Unicam 929 atomic absorption spectrometer; Philips PU 7000 plasma spectrometer; Milton Roy spectronic 3000 array spectrophotometer; Metrohm 646 VA-processor coupled to a 647 VA-stand, with a hanging mercury drop electrode, saturated Ag/AgCl (3 mol L^{-1} KCl) reference electrode and a platinum auxiliary electrode; high-pressure liquid chromatograph (HPLC) with a μ-Bondapak C-18 column (3.9 × 300 mm), a 996 photodiode array detector, an injector 717 and two 510 pumps and a cryogenic bath (Haake E. 1).

Reagents

Nitric acid, 65% (Merck; suprapur); sulphuric acid, 95–97% (ISO Merck, pro analysi); Hydrogen peroxide, 30% (Merck; suprapur); ICP multi-element standard solution IV (Merck) and Milli-Q water.

Sampling

The samples were obtained from a local store.

Procedures

In all cases a volume of approximately 23 mL was transferred to the closed vessel, and a program was run in the microwave oven at 40% power, maximum pressure 100 psi and 6 min duration [11] to degas the beer samples.

Table 1. Microwave program for three reactors

Steps	Reagent added	Time (min)	Power (%)	Pressure (psi)
1	3.5 mL H_2SO_4 (c) + 2 mL H_2O_2	6	50	15
2		4	50	15

Procedure (A) [11]

This procedure is described for three perfluoroalcoxy teflon vessels in a microwave oven. A program with two stages was selected to digest the sample. In the first stage, 20 mL of degassed beer was placed in each vessel and 3 mL of HNO_3 was added. The vessels were closed, and a three-step programme was set, each step at 40% power, 15 psi maximum pressure and a duration of 2 min. The vessels were left to cool in a cryogenic bath at 5 °C for 5 min. The reactors were opened, and in a second stage 2 mL of 30% H_2O_2 was added, the setting was 40% power, 20 psi maximum pressure, and 3 min. After cooling at room temperature, the vessels were opened, and the product was transferred to a 25 mL volumetric flask and diluted to volume with Milli-Q water.

Procedure (B)

This procedure is described for three perfluoroalcoxy teflon vessels in a microwave oven. The program to digest the sample consists of only one stage with two steps. In the first step, 20 mL of degassed beer was placed in each vessel, 3.5 mL of H_2SO_4 (c) and 2 mL of H_2O_2 were added. The vessels were closed, and a program was set to 50% power, 15 psi maximum pressure and 6 min. After that, the vessels were left to cool in a cryogenic bath at 5 °C for 5 min. A second step is set at 50% power, 15 psi maximum pressure and 4 min. After cooling down at room temperature, the vessels were opened, and the product was transferred to a 25 mL volumetric flask and diluted to volume with Milli-Q water. The procedure is summarized in Table 1.

Procedure (C) [3]

Transfer several glass beads and 5 mL of H_2SO_4 (c) to a 250 mL flask. Add 20 mL of degassed beer and then 20 mL of 30% H_2O_2 and heat gently until the initial reaction has ceased. Then heat until fumes of H_2SO_4 form. Should charring occur at any stage, add further 1 mL portions (not more) of H_2O_2. Digestion is complete when the fuming sulphuric acid remains colourless. If at any stage it seems that the contents of the flask may approach dryness, cool, add 2 to 3 mL of H_2SO_4 and continue. After cooling, the product was diluted to 25 mL with Milli-Q water in a volumetric flask.

Statistical Analysis

ANOVA was used for data treatment. A statistical analysis was performed with the computer software Statgraphics 5.0.

Results and Discussion

Development of a Wet Digestion Procedure in Closed Reactors Assisted by Microwaves and Metal Determination by FAAS

When determining trace metals by atomic spectroscopy (AS), it is necessary to destroy the organic

matter in order to avoid burner clogging in FAAS [11–14] or an increment in optical background in ICP-AES [9].

Wet digestions traditionally performed in open beakers on hot plates are the object of research with the aim of moving to closed reactors assisted by microwaves. The advantages of such treatments have been widely described in the literature [1, 15].

In this paper, a new digestion procedure assisted by microwaves is developed for trace metal determination in beer. It is based on one of the procedures proposed by the Royal Society of Chemistry applied to soft drinks and beers [3], which uses H_2SO_4 and H_2O_2 heating on a hot plate.

Previously, the authors had developed a method to determine trace metals by FAAS in beers [11] using HNO_3 and H_2O_2 in reactors assisted by microwaves. Based on this experience, we started treating 20 mL of beer to be diluted to 25 mL after digestion, so that the metal concentrations displayed enough sensitivity to be measured by FAAS. 3 mL of H_2SO_4 and 2 mL of H_2O_2 were added to the reactors containing the sample. The closed vessels are placed in the oven, and a program for three reactors was set with 4 steps. In all cases, the maximum pressure was set to 15 psi, and the magnetron power was run at 40%. It was set up in that way so as to avoid rapid formation of large amounts of gases [11]. The product of digestion was yellow and turbid, suggesting that the procedure was not powerful enough for our purposes. The four steps were grouped into two steps. The amount of H_2SO_4 was increased to 3.5 mL and the power to 50%. With this program the samples showed more transparency. Further increments of power (60% and 70%) did not create any advantage. Increasing the amount of H_2SO_4 was not convenient for making up the samples to 25 mL after digestion. The final procedure is summarized in Table 1. In this case, the digested samples show only a slight yellow colour and are not turbid.

We considered that they could be suitable for measurements in FAAS without problems related to undigested organic matter. First of all, we optimised all the instrumental variables for each metal with spiked digested samples. In all cases, the signals obtained were stable, and the flame showed a uniform behaviour.

The repeatability of the results was evaluated with 11 replicates of digested beer samples. The RSD% for Mn was 2.9, 4.7 for Cu and 10.6 for Fe. They were stable for at least one week. In order to check the influence of the matrix on the signals obtained by FAAS, the calibration curve method with inorganic aqueous standards was compared to the standard addition method. The results obtained are shown in Table 2. As observed, the optimized instrumental conditions for the samples are not adequate for measuring the metals in aqueous solution, since the slopes in the second case are too low. Therefore, the matrix remaining after digestion affects the signals. Only Mn shows a similar behaviour in both cases. This can be explained by the fact that it is the only one not associated with the compounds remaining in the matrix. It is in accordance with the results obtained for speciation of Cu, Mn and Fe in beer, in which the polymeric phenols or phytic acids are the ligands responsible for complexation of Fe and Cu [16]. In fact, Fe^{3+} forms complex compounds with polyhydroxylated organic matter and with ''ferron'' (7-iodine 8-hidroxiquinolein 5-sulphonic) [17]. In our opinion, the digestion procedure does not eliminate the possible compounds able to complex Fe. As multielemental standards are used for metal additions, we propose the standard addition method to determine Fe, Cu and Mn.

Table 2. Equation for calibration curve method and for standard addition method

	Calibration curve	Standard addition
Mn	$Y = 0.256x + 0.0014$ $R^2 = 0.9998$	$Y = 0.227x + 0.029$ $R^2 = 0.9996$
Fe	$Y = 0.0571x + 0.0025$ $R^2 = 0.9990$	$Y = 0.103x + 0.021$ $R^2 = 0.9930$
Cu	$Y = 0.08111x + 0.000$ $R^2 = 0.9956$	$Y = 0.185x + 0.0068$ $R^2 = 0.9980$

Comparison of Sample Preparation Procedures for FAAS and ICP-AES by Analysis of Variance

Three procedures based on wet digestion are compared for the determination of Fe, Cu and Mn. All of them are described in Section 3.1. That way the influence of the reagents and heating system can be investigated.

The lager beer type was chosen to compare procedures, since it is the kind most widely consumed. Cans of ''Cruzcampo'' and ''Heineken'' were purchased at local stores.

Fe, Cu and Mn were determined by triplicate by FAAS in the digested samples. An air–acetylene flame was used for the three metals. The results are shown in

Table 3. Metal concentrations (mg L^{-1}) by FAAS (means and % RSD*)

	Fe	Cu	Mn
Cruzcampo beer			
Procedure A	0.145	0.033	0.155
	15.60*	1.74*	0.98*
Procedure B	0.204	0.038	0.141
	11.80*	4.55*	4.26*
Procedure C	0.151	0.033	0.155
	2.50*	14.30*	6.70*
Heineken beer			
Procedure A	0.862	0.040	0.073
	1.92*	5.20*	2.37*
Procedure B	0.727	0.043	0.074
	3.50*	6.90*	5.40*
Procedure C	0.827	0.033	0.072
	8.10*	9.39*	6.50*

Table 4. Metal concentrations (mg L^{-1}) by ICP-AES (means and % RSD*)

Cruzcampo beer	Fe	Cu	Mn
Procedure A	0.055	0.032	0.093
	7.52*	16.24*	7.53*
Procedure B	0.061	0.029	0.099
	13.2*	7.10*	3.54*
Procedure C	0.117	0.034	0.108
	32.53*	11.77*	8.97*

Table 3. The concentration means are in accordance with the values found in the literature [2, 11, 14].

Taking into account that sample preparation procedures for FAAS are often valid for AES-ICP, the same procedure comparison was evaluated by this instrumental technique for another Cruzcampo lager beer. The results obtained by ICP-AES are shown in Table 4. The mean concentration is also consistent with the bibliography. The RSD% values of the three procedures are more similar for Cu and Mn than for Fe.

One-way analysis of variance was applied to determine significant statistical differences between means for the three procedures with a confidence level of 95% ($p = 0.05$). The Tukey homogeneity test was applied to establish these differences. The results for FAAS and for ICP-AES can be seen in Table 5.

The results for Mn indicate that there are no significant differences between the procedures when the metals are determined either by FAAS or by ICP-AES. This is in accordance with the results presented in Section 3.1, in which the same slope was found for the calibration curve method and for the standard addition method. This is caused by the fact that this metal is not associated with the residual organic matter.

Table 5. Anova results and Tukey homogeneity test

		Fe	Cu	Mn
FAAS				
Cruzcampo	F	0.82	2.16	3.99
	p-value	0.4838	0.1967	0.0790
	Tukey test	–	–	–
Heineken	F	60.62	9.32	0.17
	p-value	0.0001	0.0144	0.8453
	Tukey test	B > A, C	C < A, B	–
AES-ICP				
Cruzcampo	F	6.82	1.01	3.34
	p-value	0.0285	0.4193	0.1061
	Tukey test	C > A, B	–	–

Cu does not show significant differences for the FAAS or the ICP-AES procedure, except in the case of Heineken beer subjected to FAAS, when heating is carried out on a hot plate (procedure C). This can be explained by the possible analyte loss due to its volatility when digestions are carried out in open vessels.

The Fe behaviour is more difficult to explain. It depends on the beer's nature, on the procedure and on the instrumental technique used. HNO_3 seems to be less effective in destroying the organic matter associated to Fe. Other authors [18] also report the differences in concentration found depending on sample preparation procedures.

Contribution of Different Analytical Techniques to the Investigation of Residual Organic Matter

The decomposition temperature and pressure developed in these reactors assisted by microwaves at the time of digestion is not sufficient to mineralise samples completely. In fact, these residues yield interferences in the subsequent trace metal determinations by electroanalytical techniques. In the case of HNO_3 digestion of biological materials, they can be attributed to organic compounds, especially to aromatic nitrocompounds and undecomposed macromolecules [19]. There is no detailed information about the identity of these compounds. Some authors [8] have noted that the nitric acid digests of some biological samples contain ''incomplete digestion products'' along with the inorganic species of interest. Although organic decomposition products are not usually considered as interferents for trace elemental analysis by AS

[20], other authors have stated problems, such as an increment in optical background by ICP-AES, which can cause the loss of the signal if the analytic concentration is close to the detection limit [9]. As described in sections 3.1 and 3.2, this may affect the precision and also the number of determinations that can be performed by AAS.

The use of voltammetry, liquid chromatography, spectrophotometry and classical chemical tests have allowed some authors to identify nitrobenzoic acids (NBA) as products of microwave-assisted dissolution of biological samples by HNO_3. The extreme resistance of NBA to decomposition suggests its use in the evaluation of the completeness of digestion techniques using HNO_3. The proteins in biological samples have been pointed out as the source of these undigested compounds. The dominant mechanism of attack in thermal and in microwave-assisted nitric acid is nitration of the aromatic ring followed by oxidation of the amino acid chain [8].

In the case of beer samples [21, 22] the compounds that can produce organic residues after digestion [23] are proteins that upon hydrolysis yield tryptophan and histidine and phenolic acids. Acrotoxin A [24] was found in some beers. This toxin could be a source of NBA. Tryptophan produces a mixture of aromatic compounds. Histidine gives imidazole-4-carboxylic acid. The digestion products of phenolic acids have not been reported in the literature. They could all be a source of undigested aromatic compounds after digestion.

Residual Carbon Content by ICP-AES

Studies of residual carbon content (RCC) as a means for digestion efficiency when comparing methods have been reported. It influences the precision of trace metal determination in AS and can also lead to interferences in the metal emission lines in elemental analysis [9, 10]. But on some occasions, it is also necessary to take into account the oxidation state of the carbon in order to interpret experimental results [25]. Due to the difficulty of performing elemental analysis in liquid samples together with frustrated attempts of bringing digests to dryness, the RCC was determined by ICP-AES as described in the literature [9, 20, 26]. The results obtained in $g\,L^{-1}$ were 22.0 ± 0.3 (procedure A), 16.0 ± 0.3 (procedure B), and 0.93 ± 0.03 (procedure C). Carbon standards of 0.1, 0.2, $0.4\,g\,L^{-1}$ were prepared from urea, and the wavelength used was 193.091 nm. In this case, the destruction of organic matter was more effective when heating on a hot plate in open vessels than when heating in closed reactors assisted by microwaves. This is due to the fact that in open vessels the amount of acid added can be increased without losing sensitivity. These results are in accordance with the number of measurements that can be performed with precision by the three procedures. Procedure A: 47, procedure B: 67 and procedure C: 80.

Voltammetry

Interferences found in trace metal determination using this technique encouraged us to investigate the nature of the organic residues.

Differential pulse anodic stripping voltammetry has been used previously by others to detect organic matter in food sample digestion products. Five mL of each digest is topped up to 25 mL with buffer solution NH_3/NH_4Cl of pH 9 prior to transfer into the polarographic cell [10]. The digestion performed on the hot plate (C) was not adequate to be measured due to impedance problems. This can be related to the excess of H_2SO_4 used in this procedure. The voltammogram corresponding to HNO_3 assisted by microwaves (A) showed a broad signal, and the voltammogram for H_2SO_4 assisted by microwaves (B) showed a narrower and smaller signal (Fig. 1), so that a greater amount of electroactive matter was found when HNO_3 is used. Attempts were made to identify NBA in both digested samples although the characteristic signals for NBA do not appear in any of the digests.

Differential pulse adsorptive stripping voltammetry was also applied in order to characterize the residual organic matter. The working instrumental conditions were: accumulation potential 0 V, accumulation time 2.5 min, potential scan rate $10\,mV/s$, differential pulse 100 mV. No additional information was found for the digestion products or for the NBA. Some tests were performed to check the presence of phenolic acid in the digestion products. A mixture of 15 phenolic acids usually found in beer [21, 22, 27–29] were digested by the two procedures assisted by microwaves described (A and B). In both cases, a signal is obtained between -1.2 and -2 V. The maximum for HNO_3 is $-32\,\mu A$ and for H_2SO_4 $-28\,\mu A$. Therefore, some electroactive matter remains in both digestions, but H_2SO_4 treatment is more effective. On comparing with the results obtained for the digests

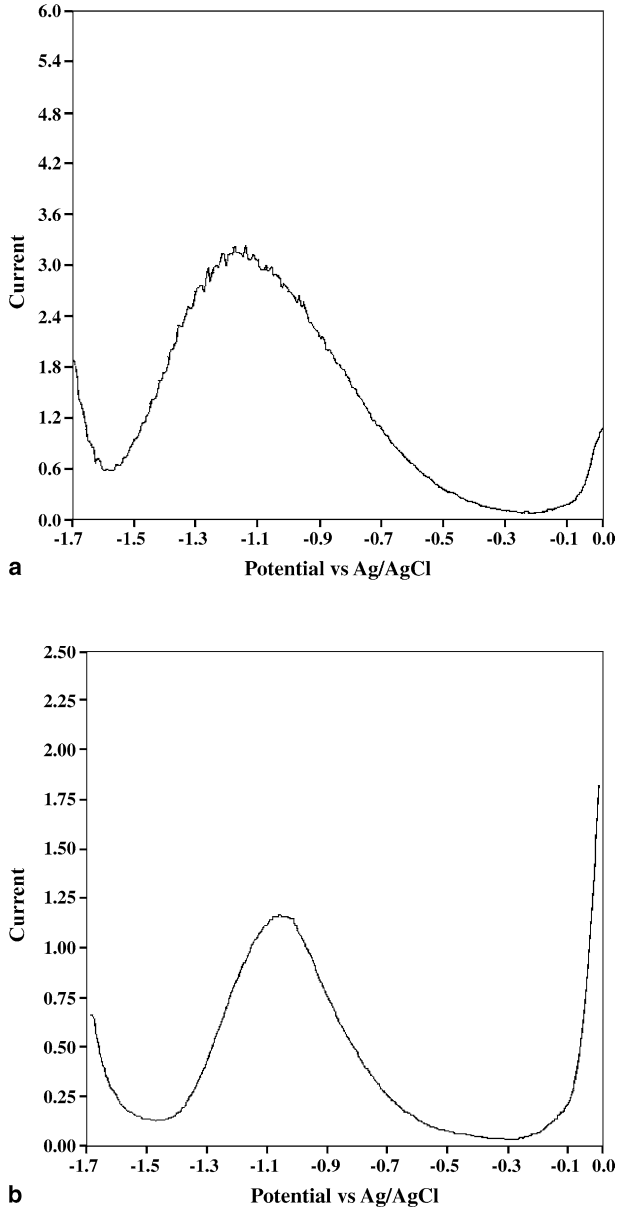

Fig. 1. (a) Voltammogram by differential pulse anodic stripping voltammetry (DPASV) of HNO_3 digest (procedure A) (b) Voltammogram by DPASV of H_2SO_4 digest (procedure B). Current (μA) versus Potential (mV)

of beer samples, we conclude that they may contain phenolic acid residues apart from other kinds of electroactive organic matter.

MIBK Extraction and UV-VIS Molecular Absorption Spectrophotometry

The potential of this instrumental technique combined with previous extraction has been used by other authors to study the organic content of the digests [8]. 20 mL of each digest was extracted with 20 mL of MIBK. The spectrum of the organic phase was run from 200 nm to 400 nm. In all cases a band was obtained. The extract of digest A showed an absorbance of 1.800 at 341 nm. Digest B extract showed an absorbance of 0.409 at 336 nm. Digest C extract gave an absorbance of 0.217 at 346 nm. These results compare well with the spectrum for NBA obtained after extraction from acid aqueous solutions ($\lambda_{max} =$ 340 nm). The main difference is that the bands are broader in the case of the beer digests. When the three digests were spiked with NBA, the corresponding MIBK extracts showed an increment in the absorbance compared to the spectrum of the MIBK extract of the digests. Therefore, we can assume the presence of NBA in all cases, and a higher one for the HNO_3 extract. Apart from that, there are possibly also other organic compounds with a similar solubility, as suggested by the difference in bandwidth described above.

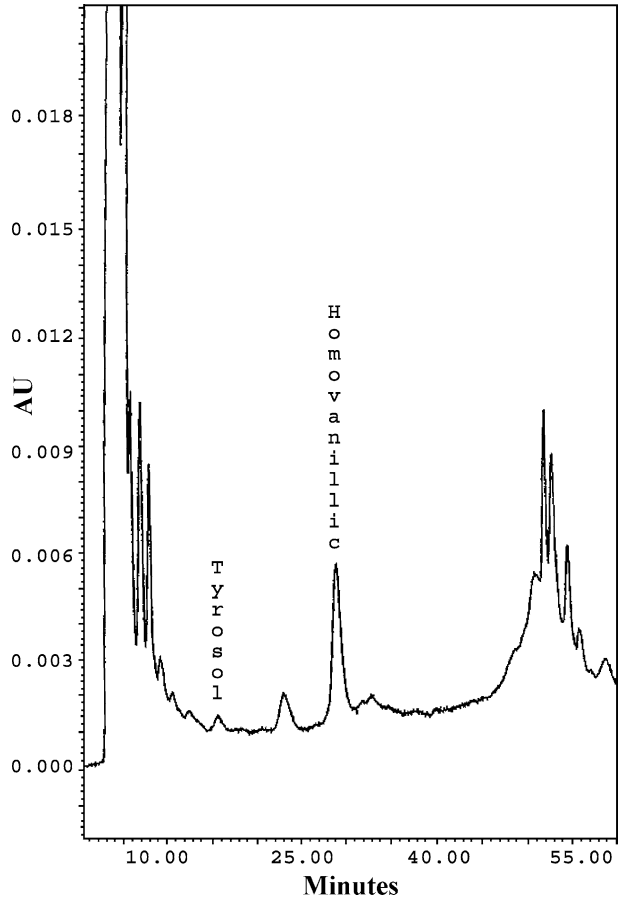

Fig. 2. Liquid chromatogram of H_2SO_4 digest (procedure B)

A mixture of 15 phenolic acids was digested using the three procedures. The MIBK extracts only showed a clear band at 333 nm for digest A, indicating the presence of some of these compounds.

HPLC Identification of Aromatic Digestion Products

With the aim of clarifying the information obtained by voltammetry and MAS, some tests were performed using an HPLC photodiode array detector. The instrumental conditions were: flow rate 1 mL/min. and volume of the sample injection loop 20 µL. The HPLC eluents were a dissolvent 1: 10% methanol, 2% acetic acid, 88% water and a dissolvent 2: 10% water, 2% acetic acid, 88% methanol.

The mixture of 15 phenolic acids mentioned above was digested using the three procedures. The digestion product was analysed by HPLC. When the digestion is carried out on a hot plate (C), all the phenolic acids are destroyed. In the case of using the microwave oven (A, B), most of them are destroyed, but some of them can be identified, e.g. tyrosol, vanillic, 3-hydroxibenzoic and protocatechin. Besides, a new group of compounds with higher polarity was detected in the HNO_3 digest.

After that, the three beer digests were analysed. Chromatographic peaks were obtained in all cases. There are more in the case of HNO_3 in microwave, followed by H_2SO_4 in microwave, and less in the case of H_2SO_4 on a hot plate. Some of these peaks are identified as polyphenols. We can conclude that some phenolic acids remain in digests A and B and that there is another source of undigested organic matter in beer (Fig. 2).

With the aim of cleaning the digestion products to identify some of the organic matter, extraction of beer digests using MIBK was carried out. They were taken to dryness with an N_2 stream and dissolved in methanol in order to be analysed by HPLC. Fewer peaks are obtained as compared to the chromatograms of the whole digests; therefore, we can say that there are residual compounds not extractable in MIBK. The extract of HNO_3 digest (A) displays a big peak at the retention time, which can be attributed to NBA. This peak does not appear in H_2SO_4 digest. It can be explained as a nitration product of residual aromatic rings produced by HNO_3. The three digestion products were spiked with 40 ppm of p-NBA. In all cases, the peak corresponding to this compound was found. In the case of HNO_3, the signal was higher due to the contribution of the NBA found during digestion.

Conclusions

Voltammetry, molecular absorption spectrophotometry and the HPLC-photodiode array detector have been used to study the residual organic matter. In all cases residual organic matter was found. NBA formed during digestion was identified in HNO_3 digest (procedure A), and residual phenolic acids remained when the digestion is performed in closed reactors with HNO_3 or H_2SO_4 (A and B).

HNO_3/H_2O_2 commonly used in sample digestions yields more residual organic matter than H_2SO_4/H_2O_2. When the latter is used, digestion is more effective in open vessels on a hot plate than in closed reactors assisted by microwaves. On the other hand, the RSD obtained for the three metals analysed is in most cases higher for the procedure on the hot plate (C) due to analyte loss and contamination. These results together with the long times required for procedure C lead to the choice of the procedures in closed reactors assisted by microwaves when trace metals are determined by AS. The dispersion of results for Fe analysed by FAAS or by ICP-AES can be attributed to associations with the residual aromatic matter. Procedures A and B are susceptible to be tested in reactors that can stand higher pressures with more drastic programs.

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