Journal of Food and Drug Analysis, Vol. 16, No. 4, 2008, Pages 30-36 藥物食品分析 第十六卷 第四期

Maltol Determination in Food by Microwave Assisted Extraction and Electrochemical Detection

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(Received: May 31, 2007; Accepted: December 25, 2007)

ABSTRACT

An electrochemical method is proposed for the determination of maltol in food. Microwave-assisted extraction procedures were developed to assist sample pre-treating steps. Experiments carried out in cyclic voltammetry showed an irreversible and adsorption controlled reduction of maltol. A cathodic peak was observed at -1.0 V for a Hanging Mercury Drop Electrode *versus* an AgCl/Ag (in saturated KCl), and the peak potential was pH independent. Square wave voltammetric procedures were selected to plot calibration curves. These procedures were carried out with the optimum conditions: pH 6.5; frequency 50 Hz; deposition potential 0.6 V; and deposition time 10 s. A linear behaviour was observed within 5.0×10^{-8} and 3.5×10^{-7} M. The proposed method was applied to the analysis of cakes, and results were compared with those obtained by an independent method. The voltammetric procedure was proven suitable for the analysis of cakes and provided environmental and economical advantages, including reduced toxicity and volume of effluents and decreased consumption of reagents.

Key words: foods, electroanalytical methods, Hanging Mercury Drop Electrode, food additive, maltol, microwave-assisted extraction

INTRODUCTION

Maltol (3-hydroxy-2-methyl-4H-pyran-4-one) (Figure 1) occurs naturally in certain conifers and was extracted firstly from larch's bark(1,2). It is present in coffee, chicory, soybeans, baked cereals, bread crusts, and caramelized and browned foods but may also be formed after sucrose pyrolysis or thermal degradation of starch(3).

In small concentrations, maltol does not have flavour on its own but modifies or enhances the inherent flavours of the food to which it is added. Thus, it is widely used as a flavour enhancer E363. It may be found among breads, cakes, malt beverages and chocolate milks. It is added in minute amounts, at levels ranging from 50 to 200 mg/kg(3). According the European law the maximum level admitted is 200 mg/kg.

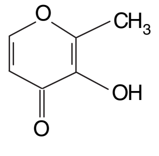

Figure 1. Structural formula of maltol.

The Food and Agriculture Organization (FAO)/World Health Organization (WHO) of the United Nations (UN) Expert Committee on Food Additives pointed out that a maximum of 2 mg/Kg of body weight *per* day is acceptable for human consumption(4). Ingestion of larger amounts may cause headaches, nausea or vomiting(5) and enhance absorption of aluminium, forming stable and neutral complexes that have neurotoxic effects(6).

Different analytical methods have been used to quantify maltol in food. These include gas chromatography (GC) using mass spectrometric (MS) detection(7-11), and liquid chromatography (LC) with diode array (DAD)(10) or amperometric detections(12). Optical methods are reported as well using UV/Vis spectrophotometry(13,14) and chemiluminescence(15). Among electrochemical techniques, the oxidation of maltol was described at silica-gel modified working(16) and/or glassy carbon electrodes(3). An indirect amperometric determination has also been tried out after reaction of maltol with a Cu(II)-phenantroline complex(17).

Previous methods are generally laborious and/or costly with tedious and complex sample preparation steps and long and excessive operator intervention. This problem is more evident for solid samples since most common analytical methodologies require mass transfer operations to a liquid phase. The analytical measure-

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ment itself should be simple and quick without the need for diverse reagents and complex unit operations.

Solid sample preparation methods are now suffering from continuous updating to obtain homogeneous and representative solutions with reduced time and costs. Several conventional solid-solvent extraction methods risk the possible loss of analyte or contamination during sample preparation, extended time required for completion of the leaching step, and consumption of large solvent volumes. Current developments are aimed at overcoming these problems, either by proposing new methods or improving the older ones. Microwave-assisted extractions (MAE) are fairly recent and enable sample preparations of reduced time and solvents. MAE is a clean process technology that is regarded as a promising alternative to classical solvent extraction techniques, reducing analysis time and the amount of organic solvents consumed, thereby minimizing the waste disposal and handling. Thus, the present work proposes MAE procedures for extracting maltol from food.

Simplification of post analytical measurements may require direct readings of the analyte. Electroanalytical approaches such as voltammetry enable such simplification and can boast the following merits: high sensitivity, low detection limit, small effect of the sample matrix (in certain instances), simple and low cost of equipment, and possible automatic on-line and portable options(18). Considering the low levels of maltol in food, it is important to use a technique of enhanced detection capabilities. For this purpose, a voltammetric determination of maltol using a Hanging Mercury Drop Electrode (HMDE) is proposed.

Thus, a MAE approach is taken to assist sample pretreating steps and the electrochemical reduction of maltol at a HMDE is investigated for the analytical step. Main analytical features are optimized and characterized, and overall procedures are applied to the analysis of samples.

MATERIALS AND METHODS

I. *Apparatus*

Electrochemical experiments were carried out in a 663 VA Metrohm system equipped with three electrodes, HMDE as working device, Ag/AgCl (saturated KCl solution) as reference unit and a glassy carbon rod as the auxiliary electrode. The electrodes were attached to an Autolab PSTAT 10 potentiostat/galvanostat running with a model GPES, version 3, from EcoChemie. Test solutions were placed in a glass crucible of 30 mL capacity. MAE procedures used a Mars-X, 1500 W Microwave Accelerated Reaction system (CEM, Mathews, NC, USA), working at 300 W and 100% capacity for three vessels (GreenChem Plus) of 100 mL capacity. Extracts were evaporated to dryness with a Buchi Rotavapor R-200, working under vacuum (Buchi Vac® V-500) and with a thermostatic bath (Buchi Heating Bath, B-490). Spectrophotometric measurements were made on a Shimadzu, UV-2501PC, spectrophotometer. The pH of buffer solutions was determined with a Sentek 71728 combined glass electrode connected to a Crison 2002 μpH meter.

II. *Reagents and Solutions*

Maltol pro-analysis was purchased from Sigma-Aldrich and used without further purification. All other chemicals were pro analysis grade (Aldrich) and all solutions were prepared using purified water (conductivity < 0.1 μS/cm) obtained from a Barnstëad E-pure 4 System. Purified nitrogen 5.0 for voltammetric measurements was obtained from Linde, Sogás.

Voltammetric trials were performed using Britton-Robinson (BR) buffer solutions of 1.9 to 12 pH. These buffers were prepared by mixing suitable volumes of phosphoric (0.16 M), acetic (0.16 M) and boric (0.16 M) acids stock solutions, and sodium hydroxide (0.8 M) solutions(19). Final ionic strength was set to 0.30 M after addition of a suitable amount of 1.34 M KNO_3 solution.

Stock standard solutions of maltol (1.0×10^{-3} M) were prepared by dissolving an exact weight of the pure solid in a small amount of ethanol and diluting up to 10.00 mL with water. Working standard solutions were prepared by accurate dilution of the previous one with suitable BR buffer. All these solutions were used for at most one week and kept in the dark at +4°C when not in use.

III. *Electrochemical Procedures*

Electrochemical behaviour was studied for a 3.0×10^{-6} M maltol solution at a HMDE using Cyclic Voltammetry (CV) and Square Wave Voltammetry (SWV) procedures. BR buffers were used as supporting electrolytes and pH adjusters, providing a 0.30 M ionic strength and pHs ranging 1.9 to 12.0. A known volume of maltol solution, together with 10.0 mL of BR buffer of suitable pH, was transferred to an electrochemical cell; concentrations of maltol ranged from 5.0×10^{-8} to 3.5×10^{-7} M. Before measurement each solution was purged with purified nitrogen for 3 minutes in the first cycle and for 30 s for each subsequent cycle. The electrode surface was automatically renewed between two consecutive scans, recorded under static conditions.

IV. *Spiked Cake Confection*

Food samples were home-made cakes made of the following ingredients: flour, water, eggs, sugar, butter, and maltol. 50 mg of maltol was added before baking at 200°C for 20 minutes. After cooled to room temperature the cake weighed 375 g, corresponding to an average of 133 mg of maltol per kg of sample. Homogenous sets of samples were obtained after grounding in a mortar and sieving in a number 10 ASTM E1 standard testing sieve of 2.0 mm.

V. *MAE Procedures*

MAE procedures were carried out with 5.000 g of grounded cake for 20.0 mL of solvent. Ethanol, ethanol/acetonitrile (1:1), hexane/acetone (1:1), diethyl ether, or water were used as solvents. Each trial was performed in triplicate. With only three vessels per run, the oven magnetron power was set to 100%, and the maximum pressure was 160 psi. The temperature increased linearly and was set constant at 85°C for 10 min; this temperature was lowered to 45°C when diethyl ether was used. 10 min was taken to reach the defined settings. Stirring in each vessel was set to medium (level 2). Vessels were allowed to cool to room temperature before opening. Extracts were filtered under vacuum with a Whatman No. 42 filter paper, and dried with a rotavapor system working under a 145 mmHg pressure and 45°C thermostatic bath. Remaining residues were repeatedly dissolved in diethyl ether prior to its analytical control. Blank assays were performed with cakes without maltol.

VI. *Conventional Sample Preparation*

30.0 g of grounded sample with 4 mg of maltol was added to 75.0 mL of ethanol, placed into a 250.0 mL Erlenmeyer flask and shaken for 2 h. NaCl solution was added to help clarification of supernatant. Resulting mixture was transferred to centrifuge tubes and centrifuged at 3000 rpm for 10 min(5). Liquid phase was separated by vacuum filtration with a Glass Microfibre paper (GF/C) and evaporated under vacuum. Resulting solid residue was dissolved again in 50.0 mL of ethanol. An aliquot of 5.0 mL was placed in a 25.0 mL Erlenmeyer flask, and completed to final volume with water. This solution presented a theoretical concentration of 16 mg of maltol/L assuming an extraction yield of 100%. Analysis of this solution was carried out using the proposed voltammetric method – 100 µL placed in 20.0 mL of suitable BR buffer – and the spectrophotometric method(14).

VII. *Comparison Method*

A spectrophotometric method was used as comparison(3,14). This method was based on the test suggested by UN Joint FAO. A coloured complex between maltol and Fe (III) formed in diethyl ether medium, and absorbance readings were taken at 540 nm. Prior to analysis, cake samples were subjected to conventional and/or microwave extraction procedures.

RESULTS AND DISCUSSION

I. *MAE Studies*

As in classic solid-liquid extractions, selection of suitable solvent(s) plays an important role at extraction efficiencies. In general, a suitable solvent should enhance the extraction of analyte and prevent its chemical alteration, and avoid co-extraction of interfering species at the same time.

Solvent choice is dictated by solubility of the analytes of interest in the solvent, interaction of the solvent and matrix, and microwave absorbing properties of the solvent converting this energy into heat(20,21). The elevated temperature of the solvent increases solubility of the analytes in the extraction solvent and also increases the desorption kinetics of the analytes from the matrix being extracted. All mass transport phenomenon are sped up at elevated temperatures and therefore influence the rates of microwave heated extraction(20).

In practice absorption is usually proportional to the solvent polarity, making water a suitable solvent for MAE extractions. It is also possible to combine solvents, in order to affect the necessary solvation characteristics and microwave heating. Association of high dielectric constant solvents, such as ethanol and acetone, with apolar solvents such as acetonitrile and hexane seems a suitable combination.

Solvents tested for the extraction of maltol from cakes were ethanol/acetonitrile (1:1), hexane/acetone (1:1) and diethyl ether. Diethyl ether is the solvent used in the classical solid-liquid extractions of maltol. Water based solvents were not considered due to the low aqueous solubility of maltol. Ethanol gave abnormally high extraction yields that could result from interfering effects upon the analytical method.

MAE experiments were always conducted near the boiling point of the acceptor medium. This prevents "auto-ignition" effects and enhances extraction efficiencies in result of increased diffusivity of the solvent into the internal parts of the matrix under high temperatures and enhanced desorption of the components from active sites of the matrix(21).

Recoveries from MAE procedures were calculated after the spectrophotometric method previously described in literature(14). Main results of extraction yields are shown in Figure 2. The amount of maltol in solvent extracts ranged from 30 to 85%, depending on the extraction solvent. Combination of hexane and acetone seemed the most suitable for extracting maltol from cakes, reaching the highest extraction levels.

Atmospheric boiling points of hexane and acetone are 56.2 and 68.7°C, respectively. When MAE is conducted in closed vessels, solvent temperatures may rise, increasing extraction efficiency and reducing extraction time. However, if microwave radiation is applied to the above solvents and placed separately in the closed vessels, acetone (polar solvent) will suffer from a significant increase in boiling point whereas hexane (a nonpolar aliphatic solvent) will not heat. Only the hexane miscible mixture heats quickly, although the heating rate and the final temperature of the solvent mixture are less than the heating rates and the final temperature of the same

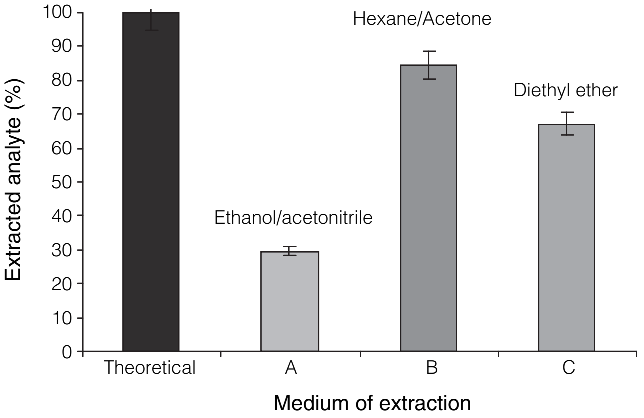

Figure 2. Yields of extracted maltol *versus* medium of extraction (n = 3).

volume of acetone alone[(20)]. The nonpolar solvent is heated in the microwave because the polar solvent heats the nonpolar solvent by conduction.

Our results indicated that addition of a nonpolar solvent will increase extraction yields. This is consistent with the low aqueous solubility of maltol. Further studies regarding longer MAE extraction and selection of alternative solvent mixtures could enhance extraction yields.

II. *Cyclic Voltammetry Experiments*

Electrochemical behavior of maltol at a HMDE was studied by cyclic voltammetry. Experiments revealed a broad irreversible wave at -1.0 V *versus* AgCl/Ag. This cathodic current resulted from the reduction of maltol at the working electrode.

Because maltol has an unsaturated carbonyl with a conjugated double bond, its electrolytic reduction may cause: (1) saturation of the double bond; (2) reduction of the carbonyl to alcohol; (3) both of above possibilities; (4) coupling of two molecules in radical form; or (5) formation of oligomers and polymers by sequential coupling. However, the corresponding reduction mechanisms for this type of chemical structure depend critically on acid-base reactions preceding, accompanying, and following electron transfer. For reduction processes occurring at pH within 5 to 7, the mechanism is confined to either a two-electron wave or two one-electron waves, as previously described[(22)]. Maltol reduction followed the first possibility. Thus, it was assumed that the only observed peak was correlated with consumption of two electrons per molecule.

Values of peak potential, E_p, were found pH independent after several cyclic voltammetric measurements taken at different BR buffers. Electrochemical transfer coefficients, αn_α, where α is the transfer coefficient and n_α is the number of electrons involved till rate limiting step, were calculated using the equation $\alpha n_\alpha = 0.048/(E_p - E_{p1/2})$, where $E_{p1/2}$ is the potential in Volts that corresponds to $i_{p/2}$. Calculated values of αn_α were 0.124. Influence of the scan rate on peak intensity, i_p, was studied within the range of 20-500 mV/s. Cathodic peaks increased linearly with the scan rate following the equation i_p ($\times 10^{-9}$ A) = 1.1×10^{-10} (scan rate, mV/s) – 7.6×10^{-11}; r = 0.997. This behavior indicated that the mass transport process was controlled by adsorption[(23)].

III. *Optimising Analytical Conditions*

Influence of pH on maltol peak shape and peak height was carried out in Square Wave Voltammetry (SWV), a more sensitive and rapid technique than other electrochemical approaches. This study was done using BR buffer solutions over a wide pH range (1.9 to 12.0) and a 3.0×10^{-6} M maltol. Voltammograms show that maltol is not electroactive in the range of pH 1.9 to 2.5, presenting electrochemical activity for pH ≥ 3.4. By increasing pH, i_p also increased until pH 6.5; from this value onwards the i_p decreased (Figure 3). Square wave studies confirmed that the E_p was independent from pH. Figure 4 shows a typical voltammogram obtained with this technique.

Experimental conditions in SWV are interrelated and have a combined effect on i_p. To establish optimum conditions for determination of maltol, the influence of frequency, *f*, deposition potential, E_d, and deposition time, t_d, on the peak height was studied by univariant procedure. Figure 3 shows the effect of the voltammetric variables in the peak current. Frequency varied from 25 Hz to 250 Hz. The i_p increased with the increased frequency until 50 Hz; above this value a decrease in peak definition was observed. So, this frequency was chosen for all subsequent measurements. Influence of

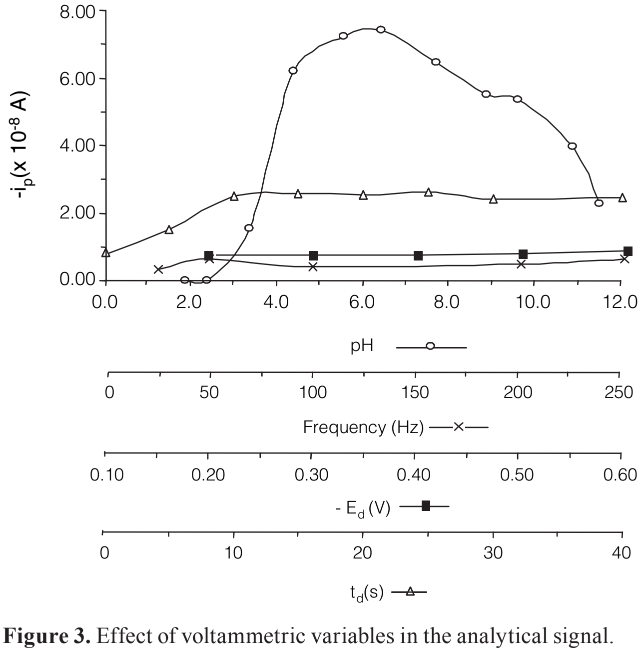

Figure 3. Effect of voltammetric variables in the analytical signal.

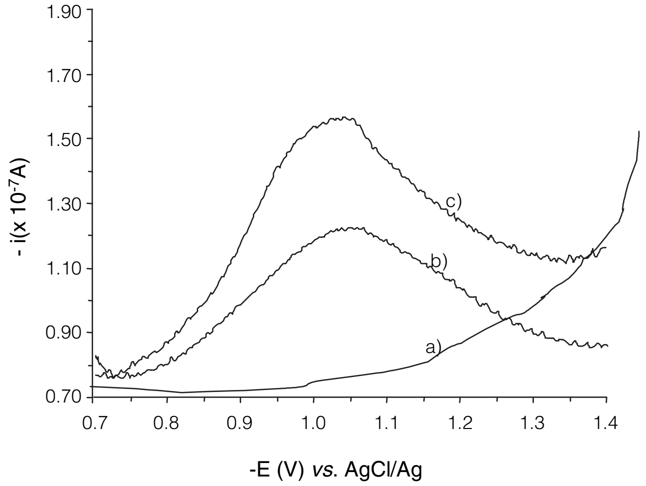

Figure 4. SW voltammograms of a) supporting electrolyte, and standard solutions of maltol in B.R. buffer with pH 6.5; b) 3.0 × 10^{-6} M; and c) 5 × 10^{-6} M.

deposition potential was studied in the range of -0.2 V to – 0.6 V *versus* AgCl/Ag. -0.6 V was chosen because it gave a higher current peak. Deposition times varied within 0 to 40 s; i_p was at its maximum after 10 s of deposition, and remained approximately constant for higher values of t_d.

With the optimised experimental conditions (pH = 6.5, $f = 50$ Hz, $P_d = -0.6$ V and $t_d = 10$ s) linearity studies were carried out for peak current and maltol concentration. Since the following linear ranges did not include the studied concentration, previous parameters were re-evaluated. This study confirmed the previously selected conditions.

IV. *Calibration Curves and Validation of Procedures*

Linear relationships between the reduction peak current and the concentration of maltol were obtained in the range 5.0 × 10^{-8} and 3.5 × 10^{-7} M. This linear behavior is described by the following equation: i_p (× 10^{-8} A) = -2.5 × 10^{-2} (±0.1 × 10^{-2}) conc. (× 10^{-8} M) -6.5 × 10^{-9} (±0.4 × 10^{-9}), with correlation coefficients higher than 0.997. Main analytical features are listed in Table 1. The limits of detection and quantification were 1.0 × 10^{-8} M and 3.3 × 10^{-8} M, respectively. These were calculated after IUPAC recommendations[(24)].

Repeatability, reproducibility, and accuracy of HMDE maltol measurements under optimised SWV conditions were confirmed after three successive determinations of two different concentrations of maltol over one day (intraday assay) and over a week (interday assay). Experiment results showed good precision and accuracy of maltol electrochemical measurements carried out in spiked blank samples (Table 2).

V. *Determination of Maltol in Cakes*

Suitability of this electroanalytical method for the quantification of maltol in foods was assessed by analyzing samples in three independent measurements by two independent methods: SWV and a spectrophotometric method (UV/Vis)[(3,14)]. The levels of maltol in cake samples are much higher than those of the linear range of the proposed method (Table 1). Thus, analysis of cakes by the proposed method requires dilution steps beforehand.

Mean values of maltol concentration and standard

Table 1. Main analytical features of HMDE method for maltol readings

Characteristics		HMDE method
LOD	*(M)*	1.0 × 10^{-8}
	(μg/L)	1.26
LOQ	*(M)*	3.3 × 10^{-8}
	(μg/L)	4.16
Linear range	*(M)*	5.0 × 10^{-8} - 3.5 × 10^{-7}
	(μg/L)	6.3 – 44.1
Slope[(a)]		-2.5 × 10^{-2} (± 0.1 × 10^{-2})
Intercept[(a)]		-6.5 × 10^{-9} (± 0.4 × 10^{-9})
R^2		> 0.997
Optimum pH		6.5
$E_p^{(b)}$ *(V)*		-1.0

LOD: limit of detection; LOQ: limit of quantification (a) Linear equation with concentrations in (× 10^{-8}) M; (b) *versus* Ag/AgCl reference electrode with saturated KCl solution.

Table 2. Analytical precision and recovery of assay of maltol by the proposed voltammetric procedure

Concentration (taken ng/mL)	Intraday[a)]				Interday[b)]			
	Found (ng/mL)	R (%)	Bias (%)	RSD (%)	Found (ng/mL)	*R (%)*	*Bias (%)*	*RSD (%)*
18.9	20.5	108.5	+ 8.5	1.4	19.9	105.3	+ 5.3	2.9
30.3	28.7	94.7	- 5.3	3.7	29.8	98.3	- 1.7	1.7

[a)] Average of three measurements over a day; [b)] Average of three measurements over a week; R: recovery; RSD: relative standard deviation.

Table 3. Determination of maltol by HMDE and spectrophotometric (UV/Vis) methods (*n* = 3)

Sample	Maltol (mg/L)		RE (%)	R (%)
	HMDE	UV/Vis		
Cake	2.83 ± 0.05	2.96 ± 0.02	-4.4	98.7

RE: Relative error; R: recovery.

deviations are presented in Table 3. Accuracy of these results was confirmed by comparison with the values obtained by the spectrophotometric method; the relative error was less than 5%. Results were precise with relative standard deviation below 4%. Recovery trials were also performed and were close to 100%.

As for analysis of the presented method, several environmental and economical aspects should be highlighted. Calibration procedures require only 20 mL of support electrolyte and the consecutive addition of only 10 to 20 µL of a standard stock solution. Each calibration is responsible for the production of less than 21 mL of effluent, carrying an amount of 0.86 mg of maltol. The reproducibility of this method also allows the consecutive analysis of at least four samples before recalibration is required. Analysis of a higher number of samples also seems possible since each drop is renewed after each signal. The mercury is recovered from solution and follows purification procedures. This provides the environmental benefits of avoiding unnecessary discharge of this toxic metal, reusing mercury and saving resources, moving experiments towards sustainable laboratory procedures.

CONCLUSIONS

Electrochemical reduction of maltol was found irreversible and adsorption controlled. Maltol determination with the HMDE based method offers low detection and quantification limits. The proposed method was precise and accurate, not affected by color or turbidity of samples as the comparison method. In addition, only 100 µL of extracted sample is required to proceed with HDME quantification. This amount is only 2% of the required volume of the spectrophotometric determination. Therefore, volume and toxicity of the emitted effluents are much lower at the proposed methodology. Time required for sample pre-treating steps may be significantly reduced from over 2 h to about 30 min after application of MAE procedures. The required 30 min includes the time taken to reach set conditions and cool extraction vessels. Extracted maltol is also increased from about 30 to 85%, when compared to conventional sample pre-treating procedures. The total volume of solvents is also reduced, achieving a reduction of 85%. Combination of MAE with HDME method presents advantages in routine applications, allowing reduced time and volume of effluents, and providing environmental and economical benefits.

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