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A *quasi* non-destructive approach for amber geological provenance assessment based on head space solid-phase microextraction gas chromatography–mass spectrometry

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ABSTRACT

Head space (HS) solid-phase micro-extraction (SPME) combined with gas chromatography–mass spectrometry (GC–MS) was used to analyze the volatile fraction of ambers of different geological origin. In particular, Romanian (romanite) and Baltic (succinite) amber samples were studied. Both types of amber have nearly similar bulk chemical compositions and could probably reflect only some differences of paleobiological and/or diagenetic origin. The present study shows that amber head space fingerprint, obtained by SPME/GC–MS, can provide a simple and *quasi* non-destructive method capable of romanite/succinite differentiation.

Among the numerous compounds present in the head space, a number of few informative variables could be selected that were able to differentiate the ambers as demonstrated by Principal Component and Cluster Analysis.

1. Introduction

Amber has been appreciated from ancient times as a precious gemstone and has been employed for the manufacture of ornaments and amulets, which are frequently found in archaeological excavations. The term 'amber' is usually used to indicate fossil resins which may, however, differ significantly in aspect, geological age, provenience, botanical designation, and chemistry. Often amber finds are indicated by mineral names such as succinite, glessite, simetite, schraufite, and so on [1].

Tracking the geological origin and establishing botanical affinities of ambers is of great importance for the comprehension of climatic/geological changes, and also for gathering information about commercial routes in antiquity. For these reasons fossil resins represent an interesting window on the past.

Although it is possible to find amber in several places across Europe, the only area that can provide amber in relatively large quantities is the so-called 'Baltic area' and Baltic amber (*succinite*) has been traded from the earliest civilizations. The fossil resin is extracted from strata dated to the Eocene on the shoreline of the Baltic Sea; the largest Baltic amber mine is in Kaliningrad (Russian Federation), but Baltic amber is also found in Lithuania, Latvia, Estonia, and Poland [2,3].

The so-called 'Amber Route', traced by archaeologists by means of mapping archaeological discoveries and literary testimonies, connecting the Baltic and Mediterranean basins, has shifted its starting point several times from the Baltic western shores to the eastern shores [4,5]; the delivery end was much more stable, to be found on the northern shores of the Adriatic Sea. The actual Romanian territory has never been crossed by the Amber Route, being some hundreds of kilometers eastwards. However, amber naturally forms on the Romanian territory, mainly in the Buzău County, around the village of Colţi, in the central-eastern area of the country. This type of amber is currently labeled *rumanite* or *romanite*. The resin bearing strata belong to the Oligocene in the Eastern Carpathian flysch and are intercalated within the lower and medium part of the lower Kliwa sandstone (0.2–1.4 m) [6].

Molecular characterization is essential for research on amber and fossil resins [7,8]. For instance, the knowledge of the chemical composition of different fossil resins has led to their categorization into different classes [9,10] and characteristic molecular marker compounds (biomarkers) may be the key indicator when determining the botanical origin [10,11].

Various analytical techniques have been applied for molecular characterization, and, in particular, for correlating the chemical composition of ambers with their geological and/or botanical origins. Characterization can be performed on the bulk material,

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on the volatile fraction, or on the extractable fraction. The most frequently used analytical techniques are gas chromatography–mass spectrometry (GC–MS), often in combination with pyrolysis (Py) [7–22], mass spectrometric techniques [23], Fourier transform infrared (FTIR) spectroscopy [24,25], Raman spectroscopy [26,27], and thermal analyses [28].

Few GC–MS studies have been specifically devoted to the distinction between Baltic and Romanian amber, *i.e*., after solvent extraction, thermal desorption (TD) or pyrolysis [13,25,29,30]. Assessment of the geological origin (Baltic area or Romania) of archaeological items has been carried out by non-destructive analytical techniques, that do not require any sampling or pre-treatment of the object, such as variable angle reflectance (VAR) FTIR spectroscopy and Fourier transform Raman (FT-Raman) spectroscopy [31–34]. However, the latter analytical techniques, although non-destructive, are not as informative as the GC–MS based methods. TD–GC–MS, in combination with FTIR spectroscopy, has also been applied on Romanian archaeological amber findings requiring relatively large sample amounts (3–10 mg) which had to be powdered for TD extraction ($T=200\,^{\circ}\mathrm{C}$) of the volatile compounds [30].

A very preliminary attempt to differentiate ambers from different origins on the base of their volatile components measured by GC–MS as an alternative of FTIR spectroscopy “fingerprinting” has been described [35]. Experimental details, however, are completely lacking and identification has been limited to a few compounds.

These findings could suggest that the head space (HS) composition (obviously enriched in volatile components) could be sufficiently informative for discrimination purposes. The best approach to sample the headspace could be solid-phase micro-extraction (SPME) coupled to GC–MS.

SPME, developed in the early 1990s by Pawliszyn [38], involves the use of a fiber coated with a liquid (polymer) or a solid (porous sorbent) extracting phase. After extraction, the SPME fiber is transferred to the injection port of a gas chromatograph, where desorption of the analytes takes place and analysis is carried out. The distinctive characteristic of SPME is that the extraction, besides being fast, simple and solventless, can be performed on liquid, solid or gaseous samples in a non-destructive way.

So far, SPME/GC–MS has been applied for differentiation of resins or gum-resins such as myrrh, olibanum, galbanum, labdanum, mastic, and conifer resins in fresh materials and in archaeological samples from ancient Egypt [36]. In another study, the same method has been used for the identification of two volatile degradation products, *i.e*., formic and acetic acid, from Baltic amber [37] but, surprisingly, no attempt has been done to fingerprint the whole head space.

In the present study amber samples of known geological origin – *i.e*, from the Baltic area (succinite) and from Romania (romanite) – were analyzed to provide a proof-of-concept that low molecular mass (LMM) analytes in the volatile fraction can provide discrimination of the two ambers. Indeed, principal component analysis and cluster analysis (performed using few representative features of the head space) showed an unambiguous separation into two distinct groups.

2. Experimental

2.1. Amber samples

Eight samples of romanite from Colţi (Romania) and six samples of Baltic amber from Kaliningrad (Russian Federation) and Poland (Table 1), provided by the National Geological Museum in Bucharest (Romania), were analyzed. The sample fragments had a weight of *ca.* 1–8 mg. The amber samples from Colţi show a high color variability from dark brown to orange, shiny or opaque, and can be considered, at least for this aspect, representative of romanite variability. Concerning the succinite samples, all of them are of controlled origin, mostly coming from Kaliningrad, which is a well recognized source for Baltic amber as reported from the early '80 by Beck [3].

2.2. HS-SPME

Some preliminary tests were performed in order to set up the HS-SPME experimental conditions, *i.e.*, choice of the fiber and of the extraction temperature. In particular, polyacrylate (PA), divinylbenzene/carboxen/polydimethylsiloxane (DVB/carboxen/PDMS), and carboxen/polydimethylsiloxane (carboxen/PDMS) fibers were tested. Extraction temperatures of 50 °C, 70 °C, and 100 °C were evaluated by taking into account both the number and abundance of compounds present in the chromatograms, and possible chromatic alteration of the samples as a measure of the invasiveness of the analytical technique. The latter parameter was monitored by performing spectrophotocolorimetric measurements of the amber fragments before and after HS-SPME/GC–MS. These preliminary tests allowed for adoption of the following experimental conditions.

A fiber with a coating made of carboxen–polydimethylsiloxane (CAR–PDMS, 75 µm, coating length 1 cm) (Supelco, Milan, Italy) was used. Before use, the fiber was conditioned in the injector of the GC system, according to the instructions provided by the manufacturer.

The amber fragment was hermetically sealed in a 2 mL screw top vial with a polypropylene hole cap and PTFE/red rubber septum (Sigma-Aldrich, Milan, Italy) and pre-equilibrated (10 min.) in a

Table 1
Amber samples analyzed with HS-SPME–GC–MS.

ID	Provenience	Color	Weight (mg)
R1	Colţi, Romania	Dark orange, shiny	3.47
R2	Colţi, Romania	Light orange, opaque	1.24
R3	Colţi, Romania	Very dark orange, opaque	3.88
R4	Colţi, Romania	Dark orange, shiny	3.88
R5	Colţi, Romania	Dark orange with light-colored inclusion, shiny	4.95
R6	Colţi, Romania	Dark brown with light-colored inclusion, shiny	2.14
R7	Colţi, Romania	Light orange with dark inclusion, shiny	4.22
R8	Colţi, Romania	Light brown, shiny	3.84
B1	Kaliningrad, Russian Federation	Light yellow, transparent, shiny	5.60
B2	Kaliningrad, Russian Federation	Light orange, semi-transparent, shiny	8.28
B3	Kaliningrad, Russian Federation	Dark orange, shiny	3.06
B4	Kaliningrad, Russian Federation	Light yellow, transparent with dark inclusions, shiny	4.53
B5	Kaliningrad, Russian Federation	Light yellow, transparent with dark inclusion, shiny	1.93
B6	Poland	Light yellow, transparent with dark inclusion, shiny	4.53

thermostatic bath at 70 °C. Then, the SPME device was inserted into the sealed vial by manually penetrating the septum and the fiber was exposed to the amber material headspace (15 min extraction time).

After sampling, the SPME device was immediately inserted into the GC injector and the fiber was thermally desorbed for 5 min at 200 °C in splitless mode. Before new sampling, the fiber was reconditioned for 5 min in the GC injector port at 280 °C in order to eliminate memory effects.

2.3. *GC–MS*

GC–MS analyses were carried out with a Finnigan Trace GC UltraGas Chromatograph coupled to anIon Trap Mass Spectrometer (Finnigan Polaris Q).Compounds were separated on a fused silica SPB-5 capillary column (30 m × 0.20 mm inner diameter, 0.25 μm coating thickness) (Supelco, Milan, Italy). The temperature program was: 5 min at 40 °C, 4 °C min^{-1} linear to 240 °C, 20 min isotherm. Helium was used as the carrier gas. Injector, transfer line temperature and ion-source temperatures were 200, 250, and 150 °C, respectively. Mass spectra (40–400 m/z) were acquired in electron ionization (EI) mode (70 eV).

2.4. *Qualitative and semi-quantitative analysis*

Compounds were identified by comparing the MS fragmentation pattern with those of literature data [8,10,11,13,15,18] and/or by National Institute of Standards and Technology (NIST) MS database search.

The relative amounts of individual components were calculated as percent peak areas relative to the total peak area of the selected compounds. Due to the low sample amounts it was not possible to carry out replica measurements. In fact, a second HS-SPME–GC–MS analysis, which implicates another heating of the sample, although performed at relatively low temperatures (*T* extraction = 70 °C), was shown to produce lower amounts of LMM compounds.

Multivariate data analysis was performed using principal component analysis (PCA) of the correlation matrix and hierarchical cluster analysis (HCA) by means of Statistica, version 10 (Statsoft).

3. Results and discussion

Samples of known geological origin – eight for Romanian amber and six for Baltic amber (Table 1) – were studied by HS-SPME–GC–MS. The chromatograms of samples R6 and B2, representative of romanite and succinite, respectively, are reported in Figs. 1 and 2. The most salient results are summarized in Table S1 (Supplementary section). For several compounds a good match was found between the acquired spectrum and the NIST library, but for various GC peaks the compound class (*e.g.*, sesquiterpenoids) could only be indicated. Many mass spectra, however, could not be assigned, but information about the main fragments and relative intensities were listed in order to allow for a comparison with non-assigned or partially assigned compounds reported in literature.

The LMM constituents of Baltic and Romanian amber mainly consist of cymenes, bornane and fenchane monoterpenoids, ionene and methylionene, and sesquiterpenoids. Very small amounts of diterpenoids are also present. Succinic acid, although occurring in relatively high amounts in these types of amber, could not be detected, probably because no derivatization was performed.

The detailed examination of our results indicates that some compounds could only be identified in Romanian amber or, *vice versa*, were exclusively found in Baltic amber. These compounds are evidenced in Table S1. In particular, 1,8-cineole (RT = 16.07 min) and the unassigned compounds at RT = 23.79 min (MI 164 m/z), and RT = 24.02 min (MI 164 m/z) were identified in almost all Baltic amber samples, but not in Romanian amber, whereas other compounds, eluting at RT = 12.03 min (MI 138 m/z), 12.88 min (MI 138 m/z), and 30.10 min (MI 206 m/z), respectively, could be evidenced in almost all samples of Romanian amber, but are absent in the Baltic ones. These compounds may act as markers for differentiation, although generally present in low amounts.

In consideration of the relatively low abundance of these possible marker compounds to be used for discrimination, an alternative approach was attempted. Ten LMM volatile compounds (*i.e.*, carane, camphene, exo-isocamphane, endo-isocamphane, *m*- and *p*-cymene, *o*-cymene, fenchone, fenchol, camphor, borneol), eluting between RT = 12.4 min and RT = 21.4 min, were selected for semi-quantitative analyses. These compounds were sufficiently abundant in most samples and could be unambiguously identified on the base of the mass spectra and comparison with literature data. For each compound the peak area was calculated by using the single ion chromatogram (SIC) of the base peak since the intensity of the

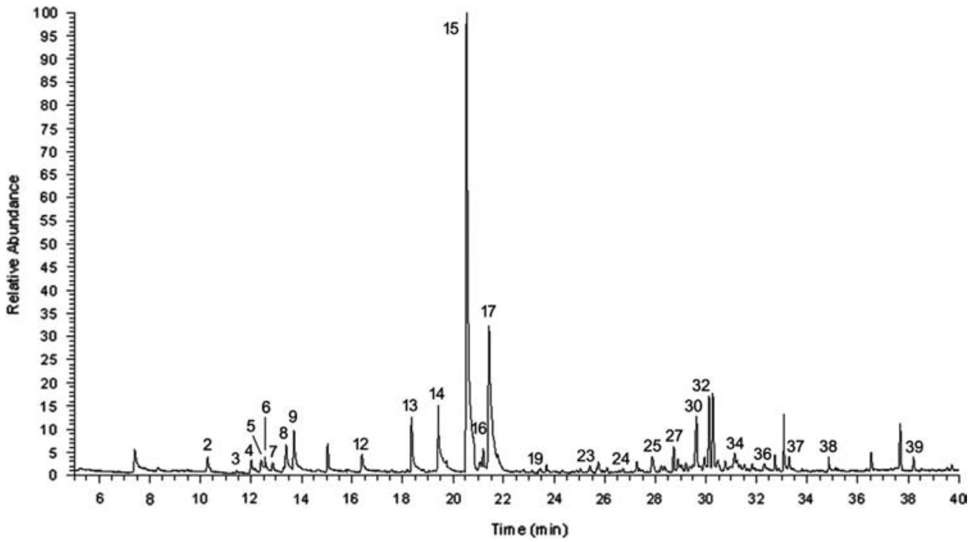

Fig. 1. HS-SPME–GCMS trace (TIC) of sample R6 (Romanian amber). Peak annotation, see Table S1.

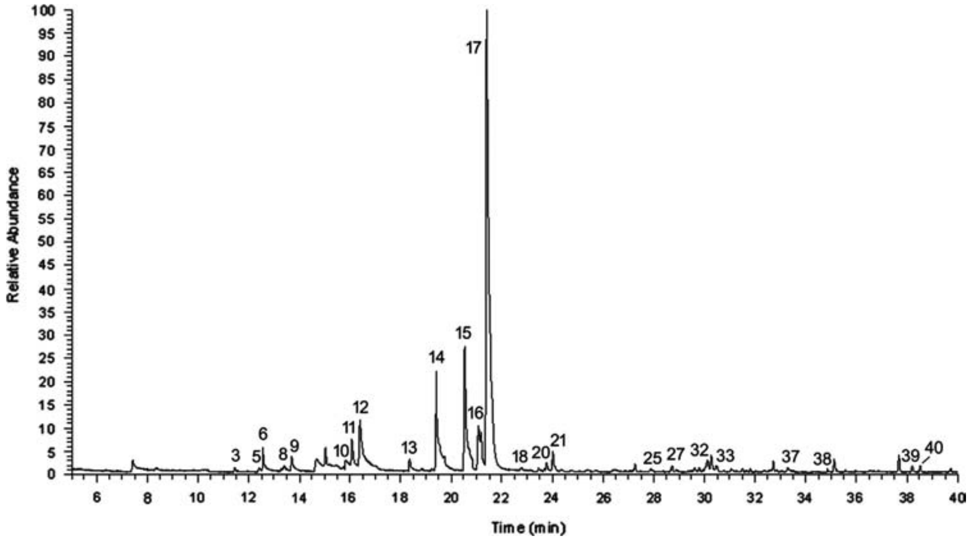

Fig. 2. HS-SPME–GCMS trace (TIC) of sample B2 (Baltic amber). Peak annotation, see Table S1.

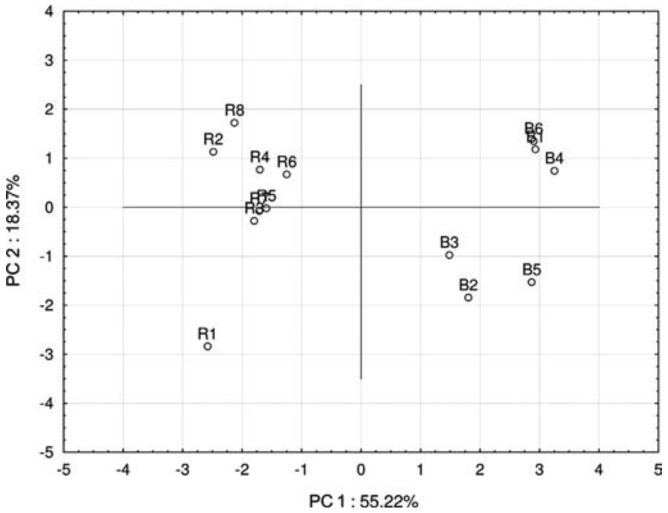

Fig. 3. PC1–PC2 score plot: Romanian amber (R1–R8) and Baltic amber (B1–B6) sample sets.

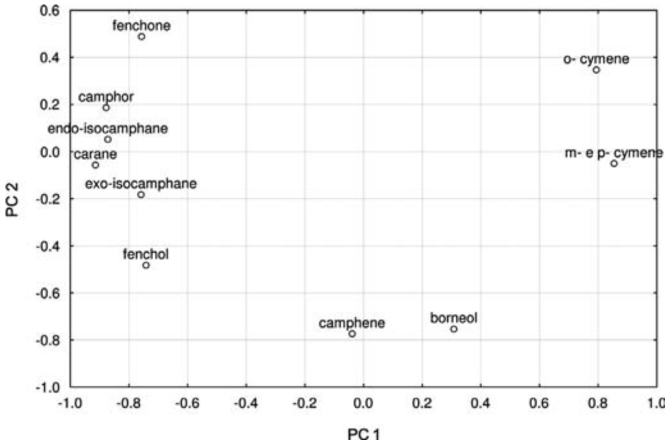

Fig. 4. Projection of the variable loadings on PC1 and PC2.

molecular ion peaks was generally low. Peak areas were normalized with respect to the total area of the ten selected compounds.

The compositional data were processed by principal components analysis (PCA) and hierarchical cluster analysis (HCA). Multivariate statistical techniques of compositional data of ambers have already been used to identify amber groups in order to establish the geological origin [29,30,39]. PCA treatment of the relative abundance data of the ten selected LMM compounds yields ten principal components (PC). The first three PCs account more than 85% of the total variance; the first PC explains 55.2% of the total variance and the second one 18.4%. These results illustrate that the considered variables are more or less correlated. Examination of the PC1–PC2 score plot (Fig. 3) shows two distinct groups: group 1 is formed by all samples of Romanian amber (R1–R8), which are characterized by negative values of PC1, whereas all Baltic amber samples (B1–B6) are located in the positive PC1 area. The projection of the loadings of the different parameters/variables on PC1 and PC2 is reported in Fig. 4. This projection shows, as may be expected, that the endo- and exo- isomers of isocamphane are somehow correlated. Moreover, the “fenchone” and “camphor” variables show similar loadings for the components 1 and 2. This might be explained by the fact that these compounds, being the ketone homologs of fenchol and borneol, respectively, are both to some extent related to the degree of oxidation of the samples. When comparing the PCA score plot (Fig. 3) and the loadings plot (Fig. 4), it comes out that the variables which seem to be mostly responsible for the separation of the romanite and succinite groups are those with the highest absolute values on PC1, *i.e.*, all variables except for camphene and borneol.

Finally, HCA performed by using the Euclidean distance and Ward's-linkage provided a dendrogram (Fig. 5) which is characterized by two main clusters: all Baltic amber samples and all Romanian amber samples. Sample R8 appeared to be somewhat different from all other romanite samples, maybe due to its higher relative content of camphor and fenchone.

These data demonstrate that differentiation between Romanian and Baltic amber may be accomplished by the determination of relative abundances of volatile compounds, thus confirming by a more systematic approach the preliminary results of a previous research [35]. Furthermore, in a study devoted to the origin of volatile compounds of succinite [40] it has been observed that prolonged heating of *Pinus* resins produces borneol, isoborneol, fenchol, and cymenes as conversion products of pinene. Fairly constant ratios of borneol, isoborneol, and fenchol have been observed. Our data are consistent with these observations and indicate that the approach used is reliable, being LMM compounds a sort of fingerprint not only of botanical origin, but also of climatic and geological changes experienced by amber.

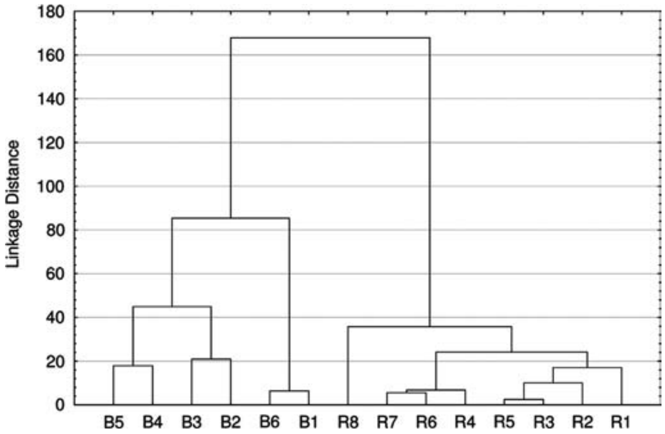

Fig. 5. Dendrogram obtained by cluster analysis using the Euclidean distance and Ward's-linkage method: Romanian amber (R1–R8) and Baltic amber (B1–B6) sample sets.

Some difficulties may arise, however, when analyzing archaeological samples. In fact, a Py–GC–MS study [12] of archaeological amber objects has allowed to classify the samples as Baltic amber on the base of “Baltic markers” such as succinic anhydride, camphene, cymenes, borneol, fenchol, and camphor, but it has been observed that the relative abundances of these volatile compounds may vary between the samples. In another study [35], however, six archaeological samples of Baltic amber of different ages were investigated and only slight differences of the volatile fraction profile, with one exception, were observed; significant differences, instead, were found between the samples of Baltic amber and samples of Sicilian and Appenine amber. Other research [21] performed on archaeological samples (Baltic amber) indicates an overall depletion of free diterpenes due to degradation phenomena, especially on the surface of amber artefacts, but apparently no changes in the first part of the chromatograms were noticed.

Concerning the issue of paleobiological and/or diagenetic differences between Romanian amber and Baltic amber, the determination of the relative abundances of some of the selected molecules seems to provide interesting information. In fact, the relative amounts of camphor and its corresponding alcohol borneol as well as of fenchol – an isomer of borneol – and its related ketone fenchone were found to change, suggesting a higher degree of oxidation for Romanian amber with respect to Baltic amber. These results seem to confirm the conclusions of Stout et al. [13] of being Romanian amber in fact a Baltic amber that has suffered partial thermal degradation.

4. Conclusions

The data as obtained by HS-SPME–GC–MS analysis of the LMM compounds of Baltic and Romanian amber seem to allow for a distinction between these types of amber despite of their similar chemical composition. Differentiation may be accomplished by combining the individuation of marker molecules with the determination of relative abundances of specific volatile compounds followed by multivariate statistical analysis.

The results are quite promising and encourage the application of this *quasi* non-destructive technique to archaeological samples and other types of amber. In fact, the applied method might be considered *quasi* non-destructive since a fraction of non-bonded volatile compounds evaporates, but no change of appearance, as determined by colorimetric measurements, is induced and sample integrity is substantially guaranteed. In this study amber fragments were used as such because already available, for archaeological items, however, no fragmentation or powdering is required since SPME can be accomplished directly on the object by creating appropriate sealing conditions.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.11.051.

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