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Rapid desorption electrospray ionization-high resolution mass spectrometry method for the analysis of melamine migration from melamine tableware

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ABSTRACT

Migration of melamine into foods from melamine tableware has been object of recent Rapid Alert System for Food and Feed (RASFF) notifications. In this context, a rapid and sensitive desorption electrospray ionization-high resolution mass spectrometry (DESI-HRMS) method was developed and validated for the determination of melamine migration from plastic materials. The migration test was performed using acetic acid 3% (*w*/*v*) as food simulant.

Evaluation of DESI parameters in terms of choice of support, motion profile, geometrical configuration and operating conditions coupled to the use of an orbitrap mass analyzer allowed to achieve significant improvements in terms of selectivity and accuracy obtaining detection and quantitation limits at low microgram per kilogram level. A LC–ESI-MS method was also developed for confirmatory purposes. Both methods were applied to 44 melamine tableware samples available on Italian market in order to assess their compliance with the law. Different concentration levels ranging from 0.00773 ± 0.0006 to 3.0 ± 0.1 mg/kg were found after the third exposure to the simulant in new and used tableware with two samples out of 44 being characterized by a melamine release higher than the legal limit, i.e. 2.5 mg/kg. A two tailed *t*-test allowed to assess the good agreement between the quantitative results obtained applying the DESI-MS method with those provided by LC–ESI-MS, thus proving reliability of DESI-HRMS as rapid technique for the study of melamine release from plastic materials.

1. Introduction

Melamine is a nitrogen-rich heterocyclic triazine used primarily in the synthesis of melamine–formaldehyde resins for the manufacture of laminates, plastics, coatings, commercial filters, glues, adhesives and moulding compounds (dishware and kitchenware) [1]. The melamine–formaldehyde polymer is ideal for food contact applications because of its hardness, heat resistance and general stability. These superior characteristics enable the repeated use of melamine-based tableware; however, repeated use can increase the possibility of melamine migration into food. In this context, legislation in the European Union was put in place to guarantee the safety of food contact materials in terms of specific migration limit setting for melamine a limit of 2.5 mg/kg [2]. Melamine has been involved also in several food recalls after the discovery of severe kidney damages in children and pets poisoned by melamine-adulterated food in which the compound was illegally added to boost the apparent protein content [3]. Owing to its high nitrogen content, melamine was also envisaged during the '50s and '60s as fertilizer for crops; in addition, it may be found in fruits and vegetables as a metabolite of the pesticide cyromazine [4]. Regarding toxicity, the International Agency for Research on Cancer stated that there is inadequate evidence for carcinogenicity in humans, but sufficient evidence in experimental animals for carcinogenicity under conditions in which melamine produces bladder calculi [5].

Finally, in April 2010, the European Food Safety Authority, in the Scientific Opinion on Melamine in Food and Feed, in accordance with the recommendations of the World Health Organization, reduced the Tolerable Daily Intake of this compound to 0.2 mg/kg of body mass [6]. The potential adulteration of food as well the release of melamine from tableware have prompted researchers to the development of different analytical methods for melamine quantitation. These methods are mainly based on liquid-chromatography both with mass spectrometric (MS) [4,7–12] and ultraviolet detection [13–16], gas chromatography–mass spectrometry [17–19] or capillary electrophoresis [20–22].

Finally, high-throughput analyses of milk and milk products were also carried out using desorption atmospheric pressure chemical ionization mass spectrometry [23], low temperature

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plasma ionization coupled with tandem mass spectrometry [24,25] and ultrasound-assisted extractive electrospray ionization mass spectrometry [26]. Ambient ionization techniques enabling the MS analysis of different samples under real native ambient conditions without sample pre-separation are of increasing interest: among them, desorption electrospray ionization (DESI) [27] has been successfully applied for analyses of forensic [28,29], pharmaceutical [30], food [31,32], environmental [33] and biological concern allowing both direct [34,35] and imaging applications [36,37].

Taking into account that melamine release from tableware has been recently object of many Rapid Alert System for Food and Feed (RASFF) notifications and that to our knowledge no data are available on the use of DESI-MS for the quantitation of this compound, in this study we propose a rapid DESI-high resolution-MS method to quantify melamine migration from different tableware samples available on the Italian market. An independent LC–MS method was also used to confirm the achieved results. The test conditions with respect to time, temperature and food simulant were in all cases in compliance with currently prescribed in the EU legislation. In addition, to acquire more knowledge of the effect of long-term use, migration tests were performed on tableware which had been used for more than 20 years. Finally, the migration pattern for short-medium term use was also investigated by performing replicate exposures applied to new sets of melamine tableware.

2. Materials and methods

2.1. Chemical and reagents

Melamine (99% purity), melamine-$^{13}C_3$ (internal standard—IS-99.8 purity, >99% isotope enrichment), potassium bromide (IR grade), acetic acid (99% purity), methanol (HPLC grade) and acetonitrile (HPLC grade) were purchased from Sigma-Aldrich (Milan, Italy). Ammonium acetate salt (98% purity) was purchased from Janssen Chimica (Beerse, Belgium). Water was obtained with a MilliQ element A10 System (S. Francisco, CA, USA). The food simulant was 3% acetic acid in water (w/v) [8,38] and its density was conventionally set to 1.0 g/cm^3.

2.2. Samples

A total of 44 new, recent and old melamine tableware of seven different brands (A–F) and sizes were collected on the Italian market. In particular, 19 new items were bought in local stores, 11 items have been used for less than 4 years and 14 items have been used for more than 20 years. Table 1 shows an overview of the analyzed samples and specimens. All the samples, excepted those 20 years old, were labeled as not for use in microwave oven. The contact surfaces of tableware were white or covered with colored decorations.

To confirm the presence of melamine plastic, transmission infrared spectroscopy (Nicolet Avatar 330 FT-IR spectrometer, Thermo Electron Corporation, Waltham, Massachusetts (MA), USA) analyses were performed on tablets prepared by mixing each pulverized sample with potassium bromide.

2.3. Specific migration test and expression of results

Migration tests were carried out according to the EN 13130-1:2004 guidelines [38]. Initially, dust was removed from tableware by wiping the sample with a lint-free cloth. Depending on the shape and type of the tableware, the migration test was performed either by immersion or by filling. Briefly, samples were exposed to pre-warmed food simulant 3% (w/v) acetic acid for 2 h at 70 °C and covered with a glass plate or aluminum foil in order to minimize simulant evaporation. This procedure was performed three times using fresh simulant and the results of the third migration was taken into account to assess compliance with the law. Small aliquots of each extracts were collected and stored at −18 °C until analysis.

For children's tableware, the actual surface area in contact with food simulant was measured and used to express the concentration of melamine in the volume of food simulant (mg/kg). For all the other samples migration was expressed in mg/kg on the basis of a surface/volume ratio of 6 dm^2/kg of food simulant [39].

2.4. DESI-HRMS analysis

Experiments were carried out using a LTQ-Orbitrap XL (Thermo Scientific, San Jose, CA) equipped with a DESI Omni Spray ion source (Prosolia, Indianapolis, IN, USA), tuned for optimum detection of the ions of interest. The DESI source was fitted with a sample platform and two video cameras to assist in the positioning and monitoring of the spray and surface. A solvent spray of methanol/water (1:1) at a flow rate of 1 μL/min was positioned 2 mm from the surface at an incident angle of 55°. The tip-to-inlet distance and the surface-to-inlet distance were set to 4 and 0.5 mm, respectively. The same configuration was used for all experiments. The nebulizing gas (nitrogen, 99.99% purity) pressure was set to 120 psi. Main experimental parameters used were as follows: spray voltage, 3.5 kV; capillary voltage, 8 V; capillary temperature, 200 °C; tube lens, 40 V. MS analyses were performed in the positive ion mode, using point to point-constant velocity (CV) motion profile at 200 μm/s with 3 mm size. Resolving power was set to 60,000 (at m/z 400). For each sample, a total of 2 μL of sample extract:methanol (1:1) was spotted on the hydrophobic DESI HTC surface Omni Slide (Prosolia Inc.) and allowed to dry at room temperature and atmospheric pressure for 30 min.

In addition to HTC Omni Slide, polymethyl methacrylate (PMMA; Prosolia Inc.) and glass surfaces (Prosolia Inc.) were also evaluated for the choice of the optimal DESI support.

Signal stability was assessed by calculating relative standard deviation (RSD%) on melamine/IS signal ratio at different melamine concentration levels (0.1, 1.0 and 2.5 mg/kg).

2.5. LC–MS and LC–MS/MS analysis

For confirmatory purposes, the results achieved using the DESI-HRMS method were compared with those obtained using an already published HPLC–MS method with minor modifications [7].

Chromatographic separation was performed on a HPLC system (Thermo Electron Corporation, San Josè, CA, USA) coupled with a LTQ XL linear ion trap mass spectrometer (Thermo Electron Corporation) equipped with a pneumatically assisted ESI interface. The system was controlled by the Xcalibur software. The mobile phase was delivered by the Surveyor chromatographic system (Thermo Electron Corporation) equipped with a 200-vial capacity sample tray. Briefly 10 μL of each extract was injected into a Luna HILIC (100 mm × 2.00 mm, 3 μm particle size, Phenomenex, CA, USA) column, thermostated at 35 °C, at a flow rate of 400 μL/min in isocratic mode for 6 min. The mobile phase consisted of 90% acetonitrile and 10% 20 mM ammonium acetate pH 3.2. The sheath gas (nitrogen, 99.99% purity), the auxiliary gas (nitrogen, 99.99% purity) and the sweep gas (nitrogen, 99.99% purity) were delivered at flow rates of 5, 0 and 0 arbitrary units, respectively. Optimized conditions of the source were set as follows: ESI voltage, 4.5 kV; capillary voltage, 15 V; capillary temperature, 350 °C; tube lens,

Table 1
Melamine migration levels from melamine tableware into 3% (*w*/*v*) acetic acid food simulant.

Sample	Usage	Type	SA:V ratio (dm^2:kg)	Exposure 1 (mg/kg)	Exposure 2 (mg/kg)	Exposure 3 (mg/kg)
Adults' use[a]						
A-3	New	Mug	9.68	1.11 ± 0.07	0.91 ± 0.03	0.98 ± 0.02
B-2	Old	Teacup	8.63	n.d.[c]	n.d.[c]	n.d.[c]
B-3	Old	Teacup	8.63	0.0056 ± 0.0003[d]	0.0040 ± 0.0004[d]	0.00773 ± 0.0006
B-4	Recent	Plate	6.00	0.38 ± 0.02	n.d.[c]	n.d.[c]
B-5	Old	Cereal bowl	8.14	0.033 ± 0.004	n.d.[c]	n.d.
B-7	Old	Plate	6.00	n.d.[c]	n.d.[c]	n.d.[c]
C-1	New	Mixing bowl	6.69	1.13 ± 0.02	0.98 ± 0.04	1.23 ± 0.03
C-3	New	Bowl	8.63	1.32 ± 0.08	1.67 ± 0.1	2.06 ± 0.04
C-5	Old	Mixing bowl	8.61	n.d.[c]	n.d.[c]	n.d.[c]
E-3	Old	Plate	6.00	n.d.[c]	n.d.[c]	n.d.[c]
E-4	Old	Coffee cup	11	n.d.[c]	n.d.[c]	n.d.[c]
E-5	Old	Plate	6.00	n.d.[c]	n.d.[c]	n.d.[c]
E-6	Old	Plate	6.00	0.014 ± 0.001	n.d.[c]	n.d.[c]
F-1	New	Milk cup	7.68	0.481 ± 0.02	0.56 ± 0.01	0.66 ± 0.05
Children's use[b]						
A-1	New	Soup bowl	7.68	0.107 ± 0.006	0.124 ± 0.006	0.12 ± 0.01
A-2	New	Plate	7.26	3.31 ± 0.06	1.61 ± 0.02	1.62 ± 0.03
A-4	Recent	Soup bowl	7.68	0.299 ± 0.006	0.447 ± 0.006	0.42 ± 0.06
A-5	Recent	Plate	7.71	0.54 ± 0.01	0.61 ± 0.01	0.8 ± 0.1
B-1	Recent	Tumbler	11.32	0.473 ± 0.007	0.590 ± 0.02	0.51 ± 0.04
B-6	Old	Cup	7.87	n.d.[c]	n.d.[c]	n.d.[c]
B-8	Old	Teacup	7.49	0.037 ± 0.005	0.0240 ± 0.002	n.d.[c]
B-9	Old	Mixing bowl	8.44	n.d.[c]	n.d.[c]	n.d.[c]
C-2	New	Cup	7.33	0.400 ± 0.004	0.56 ± 0.01	0.44 ± 0.01
C-4	Recent	Cup	7.33	0.322 ± 0.007	0.23 ± 0.01	0.314 ± 0.007
D-1[e]	New	Plastic glass	19.64	2.83 ± 0.08	2.75 ± 0.04	3.0 ± 0.1
D-2	New	Tumbler	11.17	1.88 ± 0.04	1.46 ± 0.06	1.97 ± 0.05
D-3	Recent	Soup bowl	6.67	0.358 ± 0.004	0.86 ± 0.01	0.91 ± 0.06
D-4	Recent	Plate	6.14	0.078 ± 0.001	0.153 ± 0.004	0.249 ± 0.009
D-5	Recent	Teacup	10.29	0.32 ± 0.01	0.286 ± 0.009	0.467 ± 0.006
D-6	Old	Bowl	6.15	0.0362 ± 0.004	0.15 ± 0.007	n.d.
E-1	Recent	Tumbler	10.15	0.58 ± 0.05	0.80 ± 0.06	0.86 ± 0.03
E-2	Recent	Milk bowl	6.46	0.376 ± 0.009	0.29 ± 0.03	0.40 ± 0.03
E-7	Old	Cereal bowl	6.61	n.d.[c]	n.d.[c]	n.d.[c]
F-2	New	Plate	5.91	3.13 ± 0.04	1.63 ± 0.04	1.31 ± 0.06
F-3	New	Soup bowl	6.53	1.90 ± 0.03	0.95 ± 0.06	1.61 ± 0.09
F-4	New	Cereal bowl	7.43	0.371 ± 0.009	0.61 ± 0.02	0.64 ± 0.02
F-5	New	Cup	12.37	0.59 ± 0.01	0.498 ± 0.006	0.78 ± 0.08
F-6	Recent	Tumbler	6.74	0.097 ± 0.005	0.28 ± 0.02	0.48 ± 0.04
G-1	New	Bowl	7.04	0.442 ± 0.009	0.50 ± 0.02	0.65 ± 0.07
G-2	New	Plastic glass	20.21	0.82 ± 0.08	0.92 ± 0.03	1.0 ± 0.1
G-3[e]	New	Plastic glass	20.21	2.29 ± 0.05	3.41 ± 0.08	2.85 ± 0.03
G-4	New	Bowl	7.68	1.44 ± 0.02	0.589 ± 0.03	0.79 ± 0.04
G-5	New	Plastic glass	20.21	1.55 ± 0.02	2.04 ± 0.03	1.76 ± 0.04
G-6	New	Bowl	7.68	0.63 ± 0.01	0.93 ± 0.03	1.20 ± 0.04

[a] migration expressed on the basis of a surface/volume ratio of 6 dm^2/kg of food simulant.
[b] migration expressed on the basis of the actual surface area in contact with food simulant.
[c] n.d.: not detected.
[d] concentration value determined by using HPLC–MS method.
[e] sample not compliant with the law (> 2.5 mg/kg for the exposure 3).

40 V. The mass spectrometer was operated in full scan mode (mass range: 70–200 amu).

As for LC–MS/MS, experiments were performed under both product-ion and multiple reaction monitoring (MRM) conditions using helium as collision gas. In the product-ion scan mode the 50–200 *m*/*z* range was monitored. The MRM transitions monitored were as follows: *m*/*z* 127→85 and *m*/*z* 127→109 for melamine and *m*/*z* 130→87 and *m*/*z* 130→112 for the labeled internal standard both operating with a normalized collision energy (CE) of 25.

2.6. Method validation

Validation of methods was performed according to Eurachem guidelines [40]. Acetic acid was used as the blank adding melamine-$^{13}C_3$ at the concentration of 0.1 mg/kg. Detection (y_D) and quantification (y_Q) limits were expressed as signals based on mean blank ($\bar{x}_b$) and the standard deviation of blank responses (s_b) as follows:

$$y_D = \bar{x}_b + 2ts_b,\ y_Q = \bar{x}_b + 10s_b$$

where t is the constant of the t-Student distribution (one-tailed) depending on the confidence level and degrees of freedom (d.f.). A 95% confidence level was chosen. $\bar{x}_b$ and s_b were calculated performing 10 blank measurements. The concentration values of the detection limit (LOD) and quantitation limit (LOQ) were obtained by projection of the corresponding signals y_D and y_Q through a calibration plot $y=f(x)$ onto the concentration axis.

Linearity was investigated starting from the LOQ values to 5 mg/kg (six concentration levels, four measurements at each

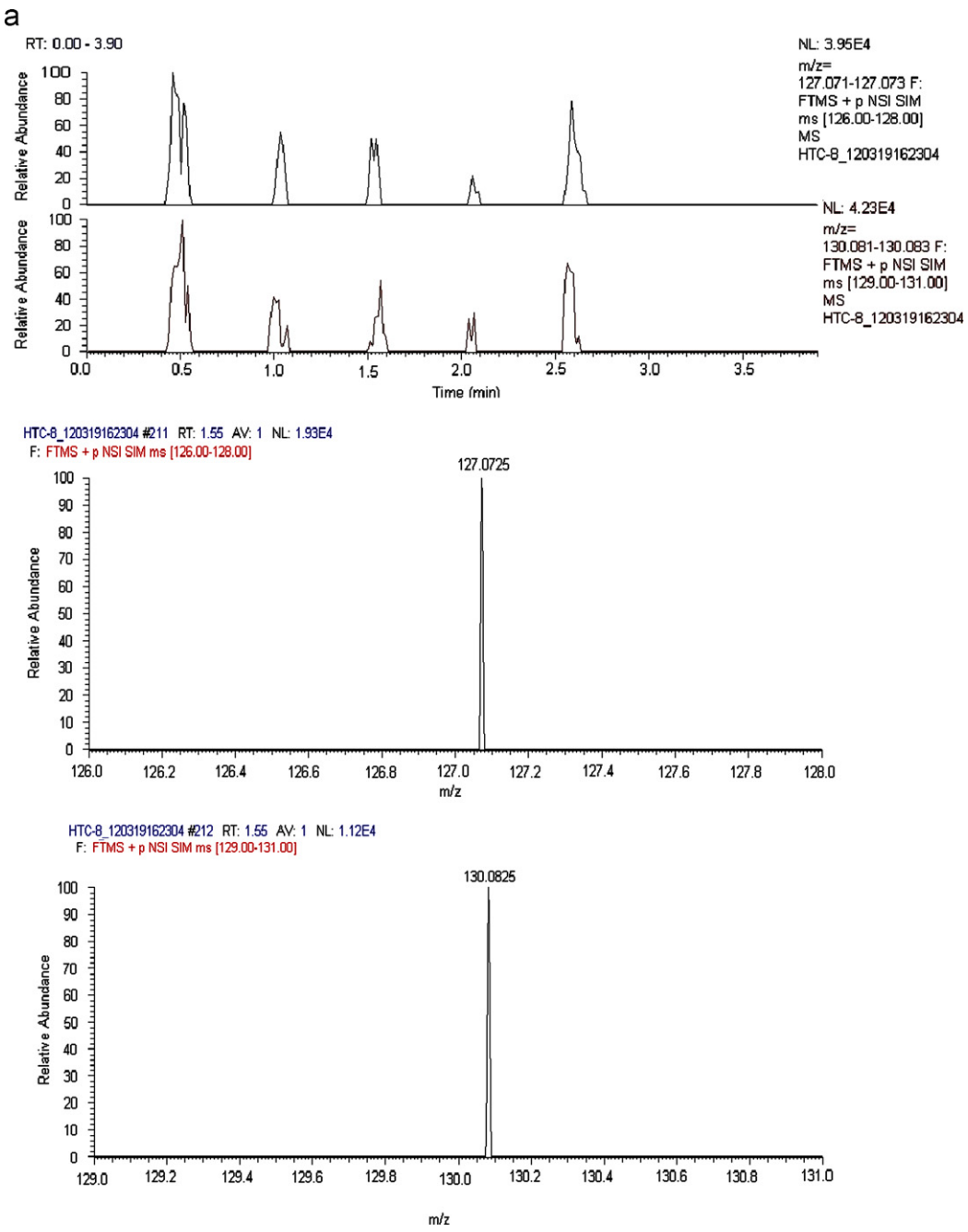

Fig. 1. DESI-HRMS analysis for (a) A-1 (exposure 3) and (b) G-2 (exposure 5) samples with the corresponding full scan-high resolution mass spectra of melamine and melamine-$^{13}C_3$ (IS).

concentration level for HPLC–MS analysis; eight concentration levels, five measurements at each concentration level for DESI-HRMS analysis). Homoscedasticity was verified by applying the Bartlett test and Mandel's fitting test was performed to check the linearity. The significance of the intercept (significance level 5%) was established running a *t*-test. Precision was assessed as RSD% in terms of intra-day repeatability and intermediate precision on two concentration levels (0.1 and 2.5 mg/kg), performing three replicates at each level. The intermediate precision was estimated over three days verifying homoscedasticity of the data and performing the analysis of variance (ANOVA) at the confidence level of 95%. Trueness was evaluated on two concentration levels (0.3 and 3 mg/kg) as percent ratio between calculated and spiked melamine amounts. All the measurements were repeated three times.

3. Results and discussion

Safety of materials in contact with food has to be evaluated as molecules can migrate from materials into food. Testing conditions should be carefully chosen in order to reflect the worst foreseeable conditions based on the use and function of the article [38]. In particular, simulant B, i.e. acetic acid 3% (*w*/*v*), has been demonstrated to be the simulant representing the worst case conditions to evaluate melamine migration from tableware [8].

3.1. DESI-HRMS method development

Taking into account the importance of using reliable methods for rapid and high throughput analysis, a method based on DESI ionization coupled with MS detection was devised for the

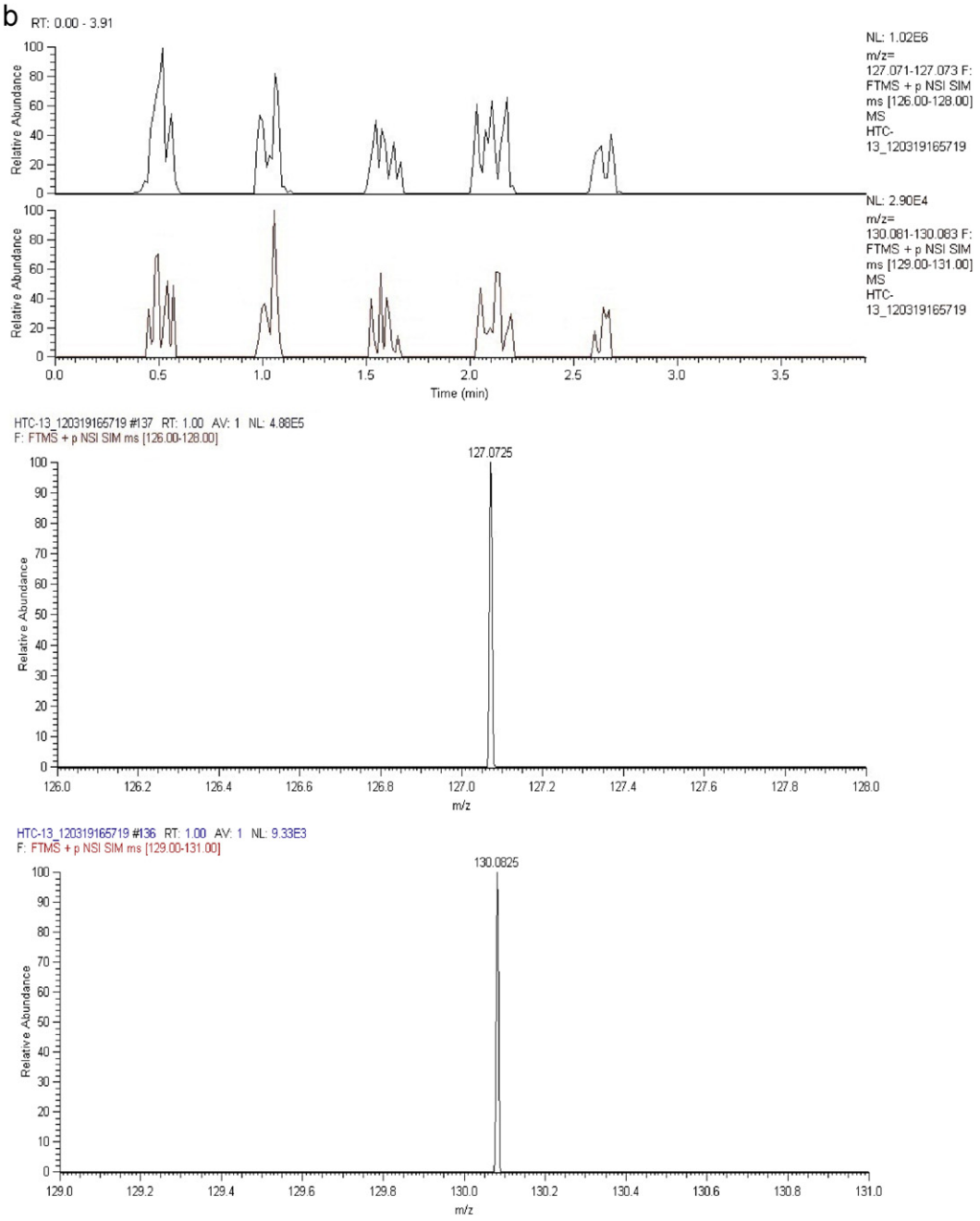

Fig. 1. Continued.

evaluation of melamine content in a food simulant after migration tests. The exploitation of high resolution MS using a LTQ-orbitrap as mass analyzer allowed to reach a very high selectivity also operating in full scan acquisition mode. Firstly, DESI parameters such as source geometry, voltages, flow rate and composition were optimized for melamine ionization. It was observed that the acidification of the spray by adding 0.1% formic acid to a mixture of methanol:water (1:1) did not significantly influence signal intensity ($p > 0.05$, two tailed t-test). Similarly, no significant differences were observed by varying the flow rate in 1–3 μl/min range.

The use of different supports and automated motion profiles was also investigated and compared in terms of signal intensity and repeatability. The HTC array surface was chosen because of its high repeatability in sample deposition, thus allowing one to obtain enhanced stability and intensity of the DESI-MS signals with RSD% always lower than 9%. By contrast, values always higher than 15% were obtained using the PMMA surfaces. Similar results were achieved also using glass slides: in fact, spotting on these supports resulted in a very slight localization of sample deposition and consequently very low signal intensities were observed.

As for the automated motion control, four different scan motions, i.e. point to point-dwell, point to point-oscillation, start point-constant velocity and point to point-constant velocity (CV) modes were evaluated. The point to point-dwell mode allowed one to stop the spray, that moves from point to point in a linear way, over each spot for a constant time (2 s). However, the motion profile being very localized, difficulties were encountered in centering the spots deposited on the sample area, obtaining

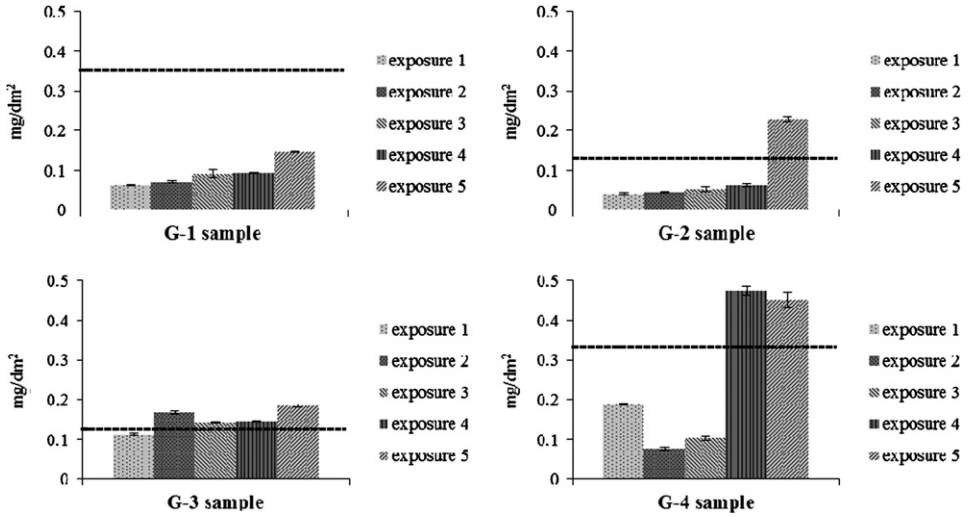

Fig. 2. Specific migration (mg/dm^2) trend for five consecutive exposures to food simulant of G1–4 samples. The dashed lines represent the legal limit (expressed in mg/dm^2) calculated by considering the real contact surface area:volume ratio for each item.

RSD of about 21%. In the case of the oscillate motion profile, in which the spray oscillates in a linear way over each spot (oscillation size, 1 mm) at constant velocity (200 μm/s) for two times, it was possible averaging over a larger surface area than in the point to point-dwell mode, but broad signals with RSD values up to 31% were observed. Finally, similar results were obtained using both the start point-constant velocity and point to point-CV modes obtaining RSD values lower than 10%. In the first case the spray moves linearly over the entire surface at constant velocity (200 μm/s rate) starting from an initial position, whereas in the latter case the spray linear scan is paused between each spot (3 mm size). However, taking into account that the point to point-CV mode allowed one to achieve more repeatable peak shapes for integration, this spray motion was selected for the analysis of tableware samples.

3.2. Method validation

The DESI-HRMS method showed good sensitivity, since LOD and LOQ values of 5.0 and 9.6 μg/kg, respectively were obtained. Linearity was proved in the LOQ-5.0 mg/kg range by applying Mandel's fitting test ($y=1.10(\pm 0.01)x$), thus attesting a linear response over about three orders of magnitude. As for method precision, good results were achieved both in terms of intra-day repeatability and intermediate precision with RSD always lower than 12%. As for intermediate precision, ANOVA performed on the data acquired over 3 days showed that the mean values were not significantly different ($p > 0.05$). Finally, the good trueness of the method was assessed obtaining values of $97 \pm 5\%$ and $103 \pm 4\%$ ($n=3$) at 0.3 and 3 mg/kg, respectively, thus proving reliability of the developed method for rapid quantitation of melamine released from tableware.

As for the LC–MS confirmatory method, LOD and LOQ values of 2.8 and 4.6 μg/kg, respectively were calculated. Linearity was proved over three orders of magnitude, in the LOQ-5 mg/kg range ($y=0.878(\pm 0.005)x$). Good precision both in terms of intra-day repeatability and intermediate precision was obtained with RSD values always lower than 6%. Trueness values of $99 \pm 6\%$ and $111 \pm 4\%$ ($n=3$) were also calculated.

3.3. Sample analysis

The applicability and reliability of the DESI-HRMS method was tested by evaluating melamine migration from 44 tableware samples of seven different brands (Fig. 1). Preliminary investigations (FTIR spectra) confirmed that all the materials were melamine-based tableware. As shown in Table 1, very different concentration levels were found in new and used tableware: more precisely, melamine was absent in the oldest (more than 20 years old) samples, thus suggesting that a continuous use of the plastic probably allowed the complete release of melamine. Regarding recent and new samples, melamine concentrations in the microgram per kilogram–milligram per kilogram range were obtained with two samples out of 44 being characterized by a melamine release higher than the specific migration limit of 2.5 mg/kg on the third exposure to simulant B. The method proved to be very specific allowing the attribution of the signal to melamine with mass accuracy always lower than 3 ppm.

Reliability of the DESI-HRMS method was also demonstrated by comparing the obtained results with those calculated using the LC–MS confirmatory method. Good agreement between data was observed: the two independent methods did not provide significant differences ($p > 0.05$, two tailed t-test).

In addition, LC–MS/MS analyses were carried out to confirm the concentration levels of melamine in the non-compliant samples.

In order to investigate the migration pattern for short-medium term use, additional experiments were carried out performing two additional successive exposures to simulant B of four new specimens of the same brand. As shown in Fig. 2, the results obtained showed an increase in melamine migration: the trend was independent from the brand, probably due to the non-homogeneity in the plastic composition between specimens.

As general comment it can be stated that despite the reduction in the specific migration limit from 30 to 2.5 mg/kg, infants and young children are highly exposed than adults when considering the exposure in relation to body weight. Fortunately, the migration observed in the present study was low compared to the current specific migration limit, thus reducing the probability of adverse effects due to the intake arising from the release of melamine plastics alone.

4. Conclusions

A DESI-HRMS method was successfully devised and applied to the quantitative determination of melamine released from melamine tableware. The method proved to be rapid, selective

and very useful for high throughput analyses as required for quality control applications. Although the analyses carried out on a representative number of samples showed that only few samples were not compliant with the law, it is important to realize that a continuous migration can take place during the whole life-time of the products, thus requiring an awareness in the daily use of melamine tableware.

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