


RESEARCH ARTICLE

A screening method for heavy metals in consumer goods using reactive desorption electrospray ionization mass spectrometry

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Rationale: Contamination of everyday goods with heavy metals such as nickel, cadmium, and lead known to be hazardous to the health of customers is an ongoing problem.

Method: Here, a mass spectrometric screening method based on reactive desorption electrospray ionization (DESI) is presented for the analysis of metals in consumer goods such as jewelry, tableware, and paintings. The method detects oxidized species of lead, nickel, cadmium, copper, and iron from the surface of objects without sample preparation. Positively charged metal ions form singly and doubly negatively charged complexes with ethylenediaminetetraacetic acid added to the DESI solvent, which are analyzed by a mass spectrometer.

Results: Qualitative and quantitative performance of the method was elucidated with metal salt standards. Subsequently, authentic samples were analyzed qualitatively. Reactive DESI-MS was able to detect lead and cadmium in eight out of nine consumer goods. For tableware, these heavy metals were found to be localized in the print as determined by reactive DESI imaging. In addition, mockup paintings generated from modern and historical pigments of Pb, Cu, Cd, and Fe in various media (acrylic binder, egg tempera, and linseed oil) were measured to show the suitability of the method for art authentication and conservation.

Conclusion: The developed method expands the range of analytes accessible by DESI-MS to metal ions. Hence, DESI becomes a suitable ionization technique for an increasing number of analyte classes, which are of interest in chemical screening of consumer goods.

1 | INTRODUCTION

The contamination of consumer goods with heavy metals hazardous to health is a known and ongoing problem.^{1,2} Jewelry containing lead, nickel, and cadmium, partially in high amounts, is only one example. In 2023 the European rapid alert system RAPEX listed 164 of such cases in the section “jewelry.” But other daily used items can also be contaminated, e.g. toys, headphones, flip flops, and tableware. Here

heavy metals are mainly found in the metal parts, but also in paints used to color the product.³ The uptake of oxidized heavy metals via the skin can cause allergic reactions or cancer, damage of the organs and harm unborn.⁴⁻⁷ To avoid negative health effects for consumers, as many products as possible should be screened for heavy metals by the legal authorities and ideally from the importing company. X-ray fluorescence analysis (XRF) is the method of choice for elemental screening of consumer goods on site (e.g. country borders), since

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portable XRF analyzers are available at reasonable cost, need minimal sample preparation, and are suited for high-throughput analysis.^{8,9} Detection of heavy metals above the legal limit by XRF screening, however, needs to be verified by certified laboratories using more sophisticated and quantitative methods including time-consuming but standardized sample preparation.³

In the last few years we have been developing methods, mass spectrometric instrumentation, and software for on-site-screening of consumer products with the goal to provide a tool which is able to screen various non-volatile substance classes from a diversity of consumer goods. Starting with a prototype of a miniaturized mass spectrometer we developed a portable self-sustaining platform featuring two ambient ionization sources: desorption electrospray ionization (DESI) and liquid extraction pen (LEP).¹⁰⁻¹⁵ We demonstrated that this setup can be used to detect non-volatile pesticides from fruit and vegetable peels, phthalates from plastic surfaces, organic substances from skin, and medical pills in a qualitative and (semi)-quantitative manner.¹⁰⁻¹⁵ Further we showed that the setup is suited for food authentication at the species level.¹³ We adapted the software of the miniaturized mass spectrometer to allow for automated compound analysis or automated food classification based on corresponding databases. This allows untrained users to perform analysis.

To expand the portfolio of application fields of the setup we aimed in the work reported here to develop a method for the analysis of heavy metals in consumer goods. The ionization methods DESI and LEP can solve analytes from the surface and ionize them by a process similar to electrospray ionization.¹⁵⁻¹⁷ Heavy metal cations produced by oxidation, e.g. by light, sweat or during production, can be desorbed by DESI and LEP.⁷ Cadmium, nickel, and lead are most stable when doubly charged leading to low m/z values. These values are too low for detection using a miniaturized ion trap mass spectrometer (m/z range 70–800) and modern laboratory-based ion trapping mass spectrometers (m/z 50–2000). To circumvent this problem and to enhance specificity a reactive DESI approach was chosen aiming for the complexation of the metal ions with a chelating agent such as ethylenediaminetetraacetic acid (EDTA). In reactive DESI the reaction agent is mixed into the solvent which is sprayed onto the sample surface.¹⁸ Reaction takes place on the surface and in the secondary droplets leaving the surface. Reaction rates are believed to be higher in secondary droplets due to the small volume.¹⁹ In 2015, Lebeau et al mixed Fe(III) into a DESI solvent to analyze EDTA in concrete showing that the intended approach is feasible.²⁰ Here we show that EDTA added to a DESI solvent can be used to qualitatively detect cations of lead, cadmium, and nickel from the surface of everyday goods such as jewelry and tableware. Results are not directly comparable with those of XRF, as both methods are surface-sensitive and non-destructive. While XRF detects all metal atoms independent of the oxidation state,²¹ reactive DESI only detects oxidized species most dangerous for consumers. Therefore, results best compare with nickel, cadmium, and lead release measurements. In addition we show that the analysis of pigments in paint is feasible with this method which may be of interest for the authentication and conservation of historical paintings.

2 | METHODS

2.1 | Chemicals

FeCl₃·6H₂O (99.5%) and NH₄OH (28% NH₃ in water) were purchased from Sigma Aldrich. Water (LC-MS CHROMASOLV) was purchased from Fluka. Cd(OAc)₂·2H₂O and Fe₄[Fe(CN)₆]₃ were purchased from Riedel da Haën. Na₂EDTA, Pb(OAc)₂·3H₂O, CuCO₃·Cu(OH)₂, PbCO₃, and methanol (Uvasol) were purchased from Merck, NiSO₄·7H₂O from Grüssing Filsum, PbS from Fisher, and CdS from abcr GmbH.

2.2 | Sample preparation

Stock solutions of iron, nickel, lead, and cadmium salts were prepared in methanol with a concentration of 20 mmol/L. Serial dilutions of 10, 5, 2.5, 1.25, and 0.63 mmol/L were prepared from stock solutions. Ten microliters of the prepared salt solution was pipetted on a solid-phase extraction (SPE) frit (PE filter for 1 mL PP columns, CHROMABOND), which was affixed onto a microscopy glass slide with double-sided adhesive tape. Each solution was soaked into the SPE frit material (diameter of 5.7 mm, 1.6 mm in height) and was allowed to dry. Several SPE frits were affixed in a row on one microscopic glass slide for method optimization and measurements of calibration curves. Authentic samples were kindly provided by the Hessian state laboratory (Giessen, Germany). Metal content of the samples was first determined using the validated methods of the state laboratory before they were analyzed with reactive DESI-MS. Validated methods included chemical pulping under pressure followed by inductively coupled plasma optical emission spectroscopy (ICP-OES). For reactive DESI-MS the whole sample or a small piece of the sample was fixed to a microscopic glass slide using double-sided adhesive tape. Pigments were mixed with paint medium linseed oil and egg tempera (egg:water 1:1) until the suspension became viscous. In addition, pigments were mixed with water (1:1), and acrylic binder was added until the suspension became viscous. Prepared suspensions were painted on filter paper and allowed to dry for a minimum of 8 weeks. Strips of colored filter paper were affixed next to each other on a glass slide and analyzed with reactive DESI mass spectrometry imaging (MSI).

2.3 | DESI measurements

DESI-MS experiments were carried out with a home-built DESI ion source coupled to an orbital trapping mass spectrometer (Exactive, Thermo Fisher Scientific GmbH, Bremen, Germany). The DESI ion source was operated at about –2 kV spray voltage, a nitrogen pressure of 6 Bar and a solvent flow rate of 2–3 µL/min. A mixture of methanol/water (1:1 v/v) with 5 mmol/L Na₂EDTA and 0.1% NH₄OH was used as solvent. The sample-to-sprayer distance was about 2 mm,

the distance between sprayer and MS inlet was about 3 mm, and the spray angle was 53° to the sample surface. The source was equipped with a computer-controlled moving stage manufactured by Danaher Precision Systems (NH, USA). The stage was operated by Servo Design Kit software V 5.22 by Galil Motion Control (CA, USA) also triggering the MS measurement. MS analysis was performed in negative ion mode in m/z range of 50 to 500. The mass resolution was set to 50 000 at m/z 200, and the obtained mass accuracy was better than ± 4 ppm using the deprotonated EDTA molecule as lock mass. In order to measure a calibration curve, the sample holder with SPE frits was moved with a fixed speed of 300 $\mu\text{m/s}$, exposing each SPE frit to the DESI spray for a defined time. If several line scans were performed on the same sample, the sample was moved toward the MS by 500 μm between lines to expose a fresh sample surface to the DESI spray. Mass spectra were recorded continuously with a fixed ion injection time of 500 ms. Authentic samples were measured the same way as the calibration curves. Calibration curves were recorded in triplicate. Reproducibility was checked on three different days. For spatially resolved DESI-MS analysis the sample surface was scanned line by line.

2.4 | Data analysis

Identities of metal-EDTA complexes were confirmed by accurate mass, isotopic pattern, and MS/MS experiments. For quantitative analysis the sum of the intensities of the singly and doubly negatively charged metal-EDTA ions was extracted from the mass spectra recorded from a SPE frit containing the metal with a known concentration and normalized to the total ion current (TIC) using Xcalibur software. For each metal concentration on the SPE frits signal intensities from 22 spectra were averaged. Each metal concentration on the SPE frit was measured three times. Calibration curves were obtained by plotting metal concentration against average metal-EDTA ion signal (normalized to TIC). Linear regression analysis was performed using the least squares method to fit a linear function and to obtain a coefficient of determination (R^2). Limit of detection (LOD) was calculated from three times the standard deviation of the regression curve's intercept and conversion to concentration via the regression curve equation. For laterally resolved analysis raw data were converted to imzML format and analyzed using the image processing software MIRION.²² Ion images of Pb-EDTA^{2-} , Cd-EDTA^{2-} , and NaHEDTA^{2-} were normalized to TIC. Bin width was set to $\Delta m/z = \pm 0.005$.

3 | RESULTS

3.1 | Optimization of the reactive DESI method

The reactive DESI conditions were optimized using SPE frits which were loaded with 10 μL of a 20 mM metal salt solution resulting in 200 nmol metal per SPE frit volume. SPE frits containing salts of lead,

nickel, iron, and cadmium were fixed in a row on top of a microscopic glass slide using double-sided adhesive tape. To test different conditions such as EDTA concentration in the spray solvent, flow rate of the DESI solvent, or spray angle several line scans were performed exposing one SPE frit after another to the DESI solvent. The stage with the samples was moved continuously, so that 15–30 spectra per SPE frit were recorded. Figure 1 shows the results using a spray solvent containing 5 mM EDTA in $\text{MeOH/H}_2\text{O}$ (1:1) with 0.1% NH_4OH at flow rate of 3 $\mu\text{L/min}$ for reactive DESI. All four metals (Fe, Ni, Cd, and Pb) formed stable metal-EDTA complexes upon reactive DESI which were desorbed into the gas phase and detected by the orbitrap analyzer in negative ion mode. Singly and doubly deprotonated EDTA ions dominated the mass spectra. In addition, several EDTA ions are present in the spectra, where one or two protons were exchanged by sodium. Nickel, lead, and cadmium, which were doubly positively charged in the salts, were detected as singly and doubly negatively charged metal-EDTA complexes. Iron which had charge state of 3+ on the SPE frit was detected as a singly negatively charged metal-EDTA complex. Table 1 summarizes for EDTA, lead, nickel, cadmium, and iron the sum formulas of the ions detected as well as their theoretical monoisotopic m/z values.

Figure 1A shows the selected ion chromatograms of the metal-EDTA complexes (sum of the monoisotopic peaks of metal-EDTA⁻ and metal-EDTA²⁻ normalized to TIC; extraction window: ± 0.02) as measured while the samples moved underneath the DESI sprayer. Normalization to the TIC accounts for DESI spray variations and was found to improve intra- and interday reproducibility. For that reason and for consistency all shown ion signals are TIC-normalized. As can be seen, the metal-EDTA complexes of iron, nickel, lead, and cadmium are found in defined time windows of about 0.4 min corresponding to time where the sprayer moved over the SPE frit with the specific salt. Figures 1B–1E show the spectra of singly negatively charged metal-EDTA complexes as they were measured by reactive DESI from the metal salt-containing SPE frits (sum spectra across the SPE frit). As shown the measured isotopic pattern of the metal-EDTA complexes fits well with the calculated pattern (shown in gray) and the mass accuracy of the measurement was better than 2 ppm.

In addition to exact mass and isotopic pattern analysis, MS/MS of the singly charged complexes was performed (Figure S1) for identification. In accordance with the literature, predominately carbon dioxide and water losses are observed. For cadmium and lead, having lower complex stability constants, a loss of the heavy metal cation can be detected. For nickel and iron, having higher complex stability constants, all fragments in the mass range up to m/z 210 have the metal still attached.

Different EDTA concentrations in the DESI solvent were tested with freshly prepared SPE frits containing the four metals. As shown in Figure S2 the highest intensities were recorded with a concentration of 5 mmol/L. Higher EDTA concentration resulted in a decrease of metal-complex ion signal intensities. For lead, highest intensities were recorded for a concentration of 2.5 mmol/L.

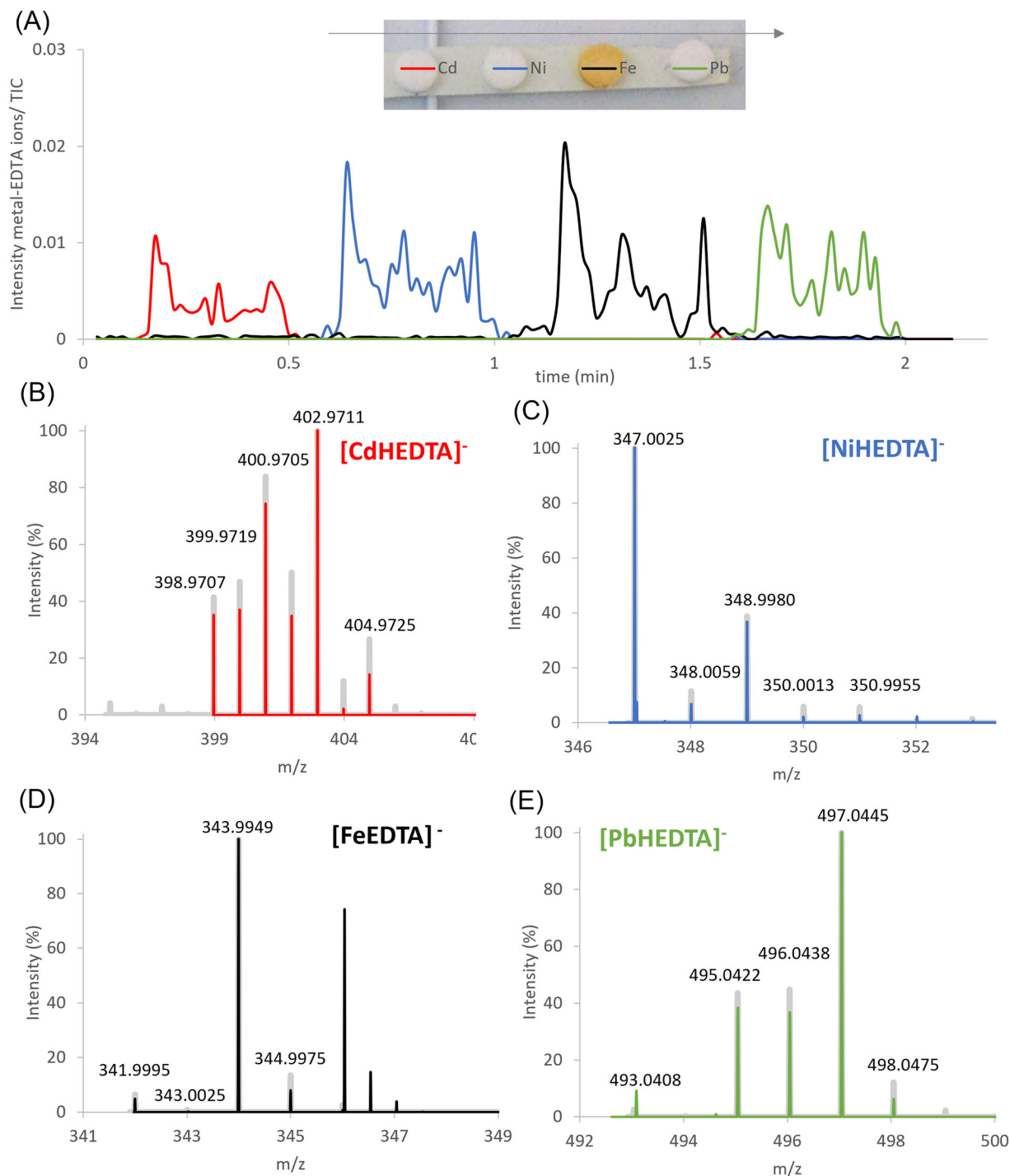


FIGURE 1 (A) Selected ion current chromatograms of the metal-EDTA complexes (sum of the monoisotopic peaks of metal-EDTA⁻ and metal-EDTA²⁻ normalized to TIC; extraction window: ± 0.02) as measured while the samples moved underneath the DESI sprayer. (B-E) Isotopic patterns of the singly negatively charged metal-EDTA complexes as they were measured by reactive DESI from the metal salt-containing SPE frits (sum spectra across the SPE frit). [Color figure can be viewed at wileyonlinelibrary.com]

3.2 | Method validation and quantitative performance

The general suitability of the reactive DESI method for quantitative analysis was evaluated using a series of metal salt solutions with concentrations ranging from 0.63 to 20 mmol/L. For all metals 10 μ L

of each salt concentration was pipetted on a SPE frit and allowed to dry. The final metal concentration on the SPE frits ranged from 0.15 to 4.9 nmol/mm³. SPE frits corresponding to a concentration series of a specific metal were analyzed in triplicate. Figure 2 displays the obtained calibration curves for lead, nickel, iron, and cadmium. As shown, a linear dependence of the intensity of the detected metal-

TABLE 1 Sum formulas and theoretical monoisotopic m/z values of the ions detected with reactive DESI-MS for EDTA and its complexes with the metals lead, iron, nickel, and cadmium.

EDTA/metal ion	Ion	Metal-EDTA complex	Theoretical monoisotopic m/z
H ₄ EDTA	H ₃ EDTA ⁻	[C ₁₀ H ₁₅ N ₂ O ₈] ⁻	291.0834
	H ₂ EDTA ²⁻	[C ₁₀ H ₁₄ N ₂ O ₈] ²⁻	145.0381
Lead	Pb ²⁺	[PbC ₁₀ H ₁₃ N ₂ O ₈] ⁻	497.0444
		[PbC ₁₀ H ₁₂ N ₂ O ₈] ²⁻	248.0185
Iron	Fe ³⁺	[FeC ₁₀ H ₁₂ N ₂ O ₈] ⁻	343.9949
Nickel	Ni ²⁺	[NiC ₁₀ H ₁₃ N ₂ O ₈] ⁻	347.0031
		[NiC ₁₀ H ₁₂ N ₂ O ₈] ²⁻	172.9979
Cadmium	Cd ²⁺	[CdC ₁₀ H ₁₃ N ₂ O ₈] ⁻	402.9711
		[CdC ₁₀ H ₁₂ N ₂ O ₈] ²⁻	200.9819

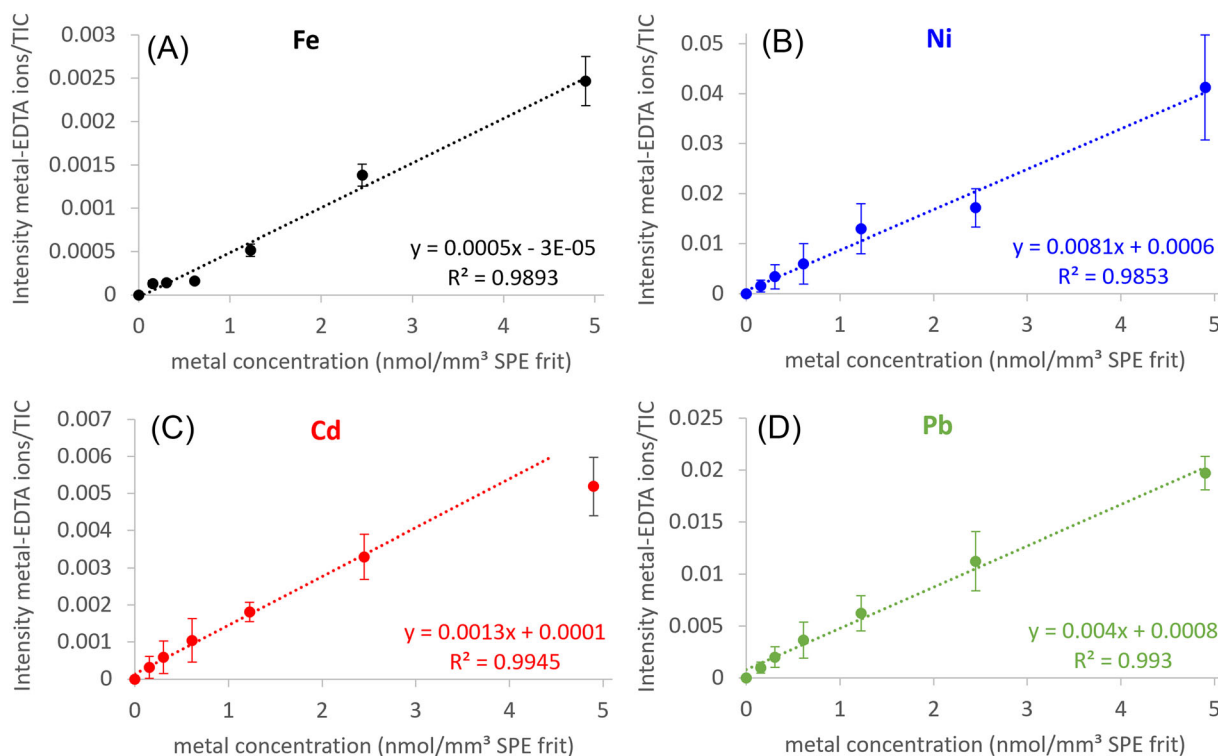


FIGURE 2 Sum of monoisotopic peaks of metal-EDTA⁻ and metal-EDTA²⁻ normalized to TIC (extraction window: ± 0.02) as obtained from three consecutive measurements on the same day by reactive DESI-MS from the metal salt-containing SPE frits (sum across the SPE frit): (A) iron (metal-EDTA⁻ only); (B) nickel; (C) cadmium; (D) lead. Error bars indicate standard deviation. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

EDTA ions on the concentration of the metal salts on the SPE frits is observed in the analyzed concentration range. The coefficient of determination ranged from 0.98537 to 0.994532. For cadmium the linear range was reduced to 2.45 nmol/mm³. LOD was 25 pmol/mm³ for cadmium, 44 pmol/mm³ for lead, 279 pmol/mm³ for nickel, and 350 pmol/mm³ for iron. However, the absolute metal ion amount sampled with reactive DESI per mass spectrum is much smaller, since metal ions are only desorbed from a spot of approximately 300 μ m in diameter from the surface of the SPE frits. Reproducibility was tested intraday (five technical replicates) and interday (3 days). The intraday reproducibility for five technical replicates ranged from 7% to 24% for the four metal-EDTA complexes over the 3 days and was on average

16% (Figure S3). The interday reproducibility was 7% for lead, 9% for cadmium, 10% for nickel, and 17% for iron (standard deviation of the mean abundance values per day). This indicates that the method in principle can give quantitative results, e.g. for samples with a metal salt distribution on a surface or a homogeneous distribution in a volume. For consumer goods quantitation, however, is difficult to implement. Since only the oxidized species on the sample surface are detectable with the method, no conclusion can be drawn concerning the total metal content, as would be needed, for example, for lead and cadmium in jewelry. In addition, the concentration of oxidized species on the surface is influenced by many factors such as production, handling, and environmental

Item	ICP-OES (mg/kg)		XRF screening (g/100 g)			Rejected
	Pb	Cd	Pb	Cd	Ni	
Ring with skull	370 000					Yes
Pendant flower	3.1		72.005			No
Pendant cross	301 000	644				Yes
Pendant penguin	2.5		11.613		50.48	No
Ring set	64.9					No
Matryoshka doll	564		0.012			Yes
Coffee cup ^a	2	0.34	1.18	0.073		Yes
Drinking glass ^a	5.6	0.47	77.458	8.743		Yes

Note: Color corresponds to analytical method: blue for ICP-OES and green for XRF.

^aValues are given as mg/piece extracted from the drinking rim.

TABLE 2 Heavy metal contents as measured with confirmatory method, ICP-OES (bulk analysis), and standard screening method, XRF (surface analysis), with the final test result regarding compliance with regulations.

conditions. Further matrix effects will have a strong influence on the quantitative results obtained. Also sample features such as material, surface hardness, surface roughness, surface planarity, and surface porosity will have a great influence on the obtained metal-EDTA ion intensities. Due to all the abovementioned limitations regarding quantitation of metal ions from surfaces of samples, it is recommended to obtain calibration curves directly from the sample, similar to a standard addition procedure, with metal salts compatible with the expected species in the sample.²⁰

In addition to SPE frits, we tested PTFE-covered diagnostic glass slides with wells of 2 mm in diameter (data not shown) as an alternative sample holder. From the PTFE-covered glass slides metal-EDTA ions were detected, but metal salt solution tended to crystallize inhomogeneously within the wells upon drying and with the given measurement conditions part of the metal salt was washed off by the DESI solvent. Therefore, the concentration dependence was not as clearly observed as for the SPE frits.

3.3 | Qualitative analysis of authentic consumer goods

In the next step the reactive DESI method was used to detect heavy metals from authentic samples. The Hessen state laboratory provided six jewelry samples, a Matryoshka doll, a drinking glass, and a coffee cup. Since the jewelry samples were small, only qualitative analysis was performed. The Hessen state laboratory uses ICP-OES as a confirmatory method after chemical pulping under pressure to determine the heavy metal content of the authentic samples (Table 2). In some cases, that laboratory also performs screening using XRF (Table 2). In all samples lead was present in different amounts ranging from 37% to 2.5 ppm. For reactive DESI-MS the whole sample or pieces of it were affixed on a microscopic glass slide and a line scan was performed over the sample. Figure 3 illustrates the results. Pictures of the whole sample are shown first and then a magnified image of the analyzed pieces. The line scan which was performed with reactive DESI-MS is shown as a yellow line. The TIC-normalized

intensity of the metal-EDTA ions is shown for lead in green, for cadmium in red, and for nickel in blue. From eight of nine samples, we were able to detect Pb-EDTA complexes. However, it is not clear if the lead cations are contaminations, which are incorporated during production or if the cations are formed by environmental influences from the metal itself. In some cases (e.g. the drinking glass and coffee cup) it is likely that the used paint contained the cations. In the case of the pendant cross we only observed Pb-EDTA ions after removing the shiny cover with sandpaper exposing the inner material. The same was true for the ring set, where we detected high signal intensities at the cutting edges. However, the opposite was observed for the pendant flower. Pb-EDTA signals decreased after removal of the white paint. For an earring in heart form (Pb content: 26 mg/kg) no Pb-EDTA ion signal could be obtained, neither on the surface nor after polishing. Possibly the lead was not present as cations in the sample and only the unoxidized metal. That the reactive DESI method is not able to oxidize elemental lead or lead alloys was confirmed using solders with varying proportions of tin (0%, 40%, 50%, 60%, and 100%). From none of the solders could Pb-EDTA or Sn-EDTA ions be generated (data not shown).

From the polished piece of the pendant cross, Cd-EDTA ions were also detected in accordance with the results from the confirmatory method. Surprisingly nickel cations were measured as Ni-EDTA ions from the surface of the pendant penguin although nickel wipe test was negative. XRF screening, however, attested high amounts of nickel in the surface layer of the pendant.

3.4 | Spatially resolved qualitative analysis of authentic consumer goods

For the drinking glass (Figure S4) and the coffee cup (Figure 4), reactive DESI-MSI was performed to determine the spatial distribution of lead and cadmium cations in the samples. For the drinking glass, the flow rate was set to 2.5 $\mu\text{L}/\text{min}$. The pixel size in the y-direction was 300 μm and in the x-direction 144 μm . A piece of glass with strawberry print was analyzed (Figures S5B and S5C). Both

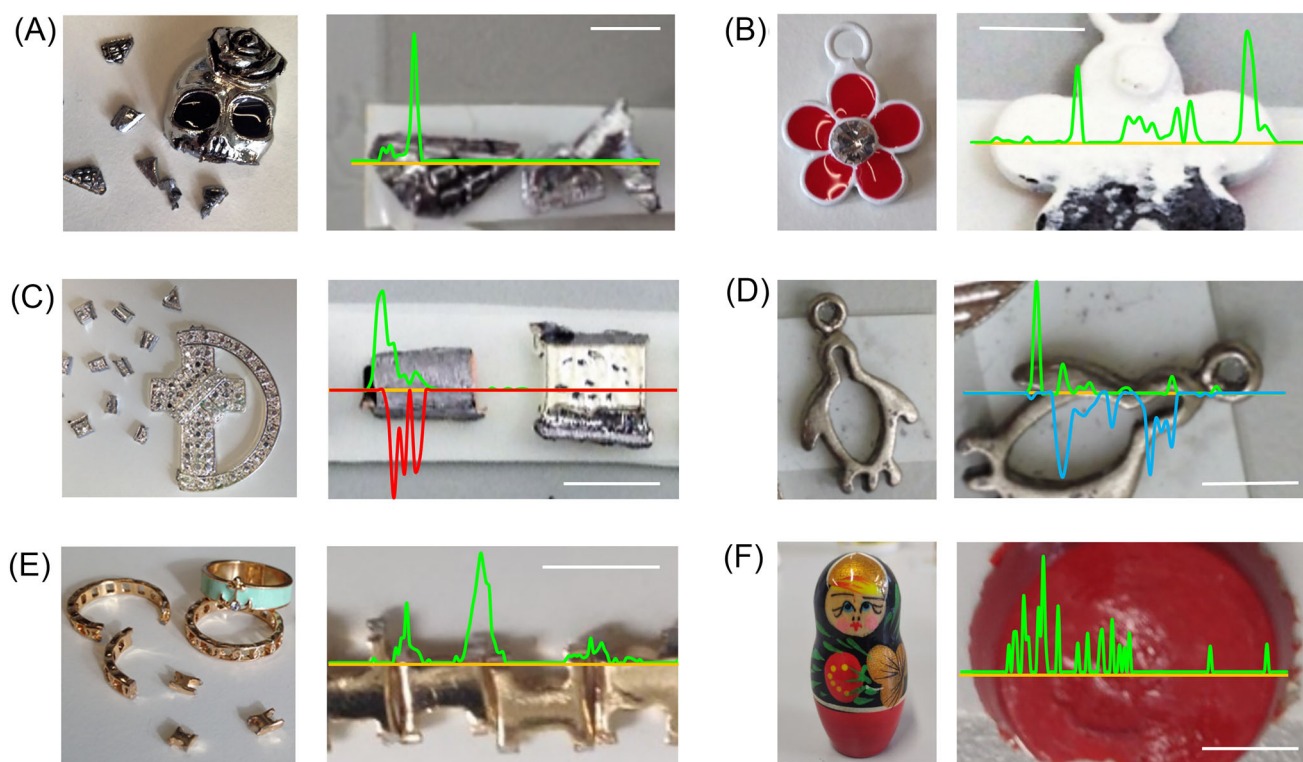


FIGURE 3 Ion chromatograms displaying sum intensity of the monoisotopic peaks of metal-EDTA⁻ and metal-EDTA²⁻ normalized to TIC (extraction window: ± 0.02) as obtained during a line scan (yellow line) across samples with reactive DESI-MS. (A) Ring with skull: Pb-EDTA (green line, max. int. 0.15). (B) Pendant flower: Pb-EDTA (green line, max. int. 0.0095). (C) Pendant cross: Pb-EDTA (green line, max. int. 0.026) and Cd-EDTA (red line, intensity increased 100 \times , original max. int. 0.00029). (D) Pendant penguin: Pb-EDTA (green line, max. int. 0.004) and Ni-EDTA (blue line, max. int. 0.003). (E) Ring set: Pb-EDTA (green line, max. int. 0.0016). (F) Matryoshka doll: Pb-EDTA (green line, max. int. 8×10^{-5}). Scale bar (white line): 5 mm. [Color figure can be viewed at wileyonlinelibrary.com]

Pb-EDTA and Cd-EDTA ions were exclusively found on the strawberry print (Figures S5D and S5F) and not on the glass itself, which is present on the top and bottom of the glass piece. However, lead and cadmium distributions showed no correlation with the print colors (red and yellow). Intensity of Cd-EDTA ions was very low (Figure S5F) compared to the intensity of Pb-EDTA ions. The isotopic pattern of Pb-EDTA²⁻ directly obtained from the imaging measurement is shown in Figure S5E. The isotopic pattern of Cd-EDTA²⁻ shown in Figure S5G was obtained from another glass piece of the same sample.

Three pieces of the coffee cup were analyzed by reactive DESI-MSI showing printed letters of different color (orange and brown) and size (Figures 4A and 4B). Pixel size set in the experiments was $100 \times 100 \mu\text{m}^2$. The hypothesis was that the heavy metals were used as pigments in the print: cadmium for orange and lead for brown. Figures 4C–4E show that the lead and cadmium distributions are clearly associated with the colors used for the letters. However, both heavy metals are found in both colors with similar ion intensities. This indicates that the heavy metals are not the major pigment of the print color, but rather an impurity of both print colors disproving the hypothesis. In general lead was found with 20 times higher intensity on average than cadmium which is in line with XRF results. XRF determined a 16 times higher lead concentration than cadmium.

3.5 | Qualitative analysis of mock-up paintings

Historically, pigments containing heavy metals were widely used in paintings. One way to verify the authenticity of a historical painting is to analyze pigments and binding medium.^{23–26} To test if the method is in principle suitable for this kind of analysis, four commonly used historical pigments and one pigment (CdS) employed in modern paintings were prepared in egg tempera, painted on filter paper, and allowed to dry for 2 months. Strips of colored filter paper were affixed next to each other (Figure 5A) and analyzed with reactive DESI-MSI (Figure 5B). As shown, complexes of the metals lead, copper, iron, and cadmium can be even detected from these highly unsolvable pigments with a spatial resolution of $100 \mu\text{m}$. In addition, media can be analyzed by changing the solvent to methanol/water (1:1 v/v) as was also shown recently by Watts and Lagalante.²⁶ Each of the three media (egg tempera, linseed oil and acrylic binder) has a distinct MS fingerprint in negative ion mode in the low m/z range (Figure S5). While linseed oil and egg tempera show a more similar profile to fatty acids and lipids as the most abundant ion species, acrylic binder shows an ion distribution typical for polymers with a mass difference of 44.0257 u, which is most likely alkylphenyl ethoxylates used in the acrylic binder. Using an EDTA concentration of 0.5 mM the simultaneous analysis of metals and binding media in a single

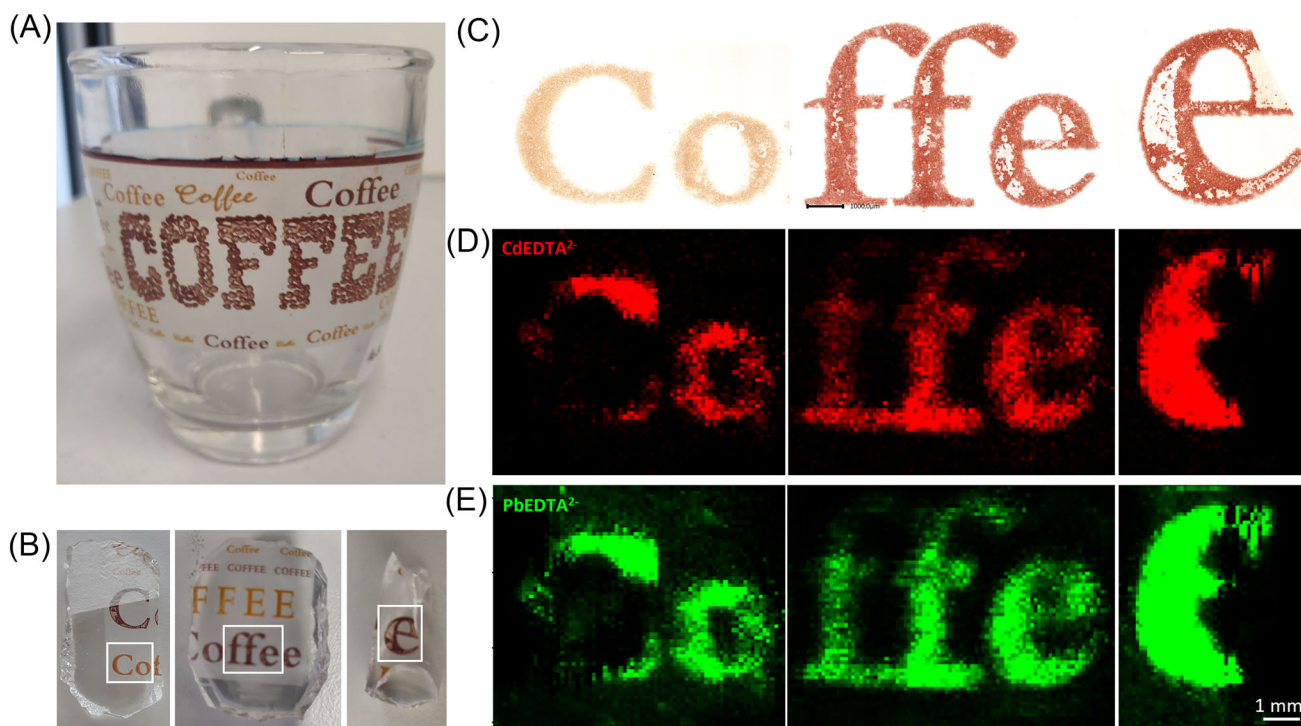


FIGURE 4 (A) Picture of the coffee cup containing lead and cadmium in the drinking rim. (B) Glass piece analyzed by reactive DESI (top view) MSI. (C) Microscope images of the analyzed sample areas. (D) TIC-normalized ion image of Cd-EDTA²⁻ (red). (E) TIC-normalized ion image of Pb-EDTA²⁻ (green). To obtain an optimal ion image quality, all detected isotopes of the metal-EDTA²⁻ (see Table S1) were summed in (D) and (E). The extraction window for each isotope was ± 0.005 m/z . To highlight pixels, where Pb-EDTA²⁻ and Cd-EDTA²⁻ were detected, maximum intensity was set to 10% for lead and 23% for cadmium of the original maximum intensity of the ion images. [Color figure can be viewed at wileyonlinelibrary.com]

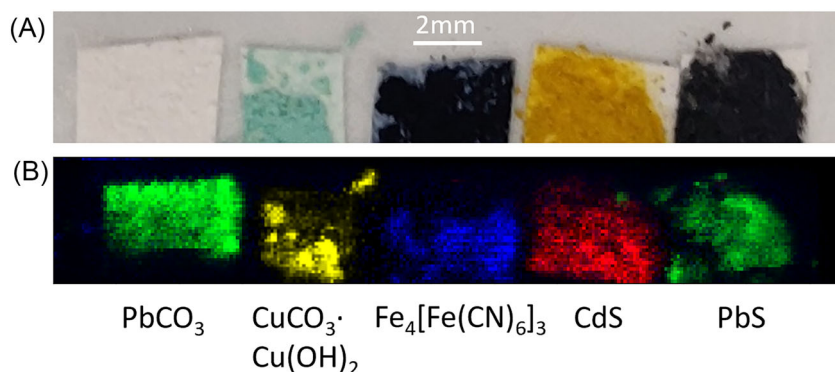


FIGURE 5 (A) Picture of paper strips colored with historical and modern pigments in egg tempera. (B) Reactive DESI-MSI: overlay of TIC-normalized ion images of Pb-EDTA²⁻ (m/z 248.018 ± 0.005 , green), Cu-EDTA²⁻ (m/z 175.4943 ± 0.005 , yellow), Fe-EDTA⁻ (m/z 343.9946 ± 0.005 , blue), and Cd-EDTA²⁻ (m/z 200.982 ± 0.005 , red). Pixel size $100 \times 100 \mu m^2$. Maximum intensity was set to 60% of the original maximum intensity of the ion images. [Color figure can be viewed at wileyonlinelibrary.com]

experiment is possible, but with lower sensitivity for both analyte groups (Figure S6).

4 | DISCUSSION

The developed reactive DESI method is a fast and easy-to-implement technique for heavy metal screening of portable medium-sized samples at existing mass spectrometers with atmospheric pressure interface. For qualitative analysis, no or minor sample preparation is needed. Samples can be held manually underneath the DESI sprayer and in such a way different parts of a sample can be analyzed very

quickly. In contrast to XRF only the oxidized metal species on the surface of the sample are accessible by the method. For consumer goods these are the most dangerous because they can leave the surface, enter the skin, and cause health problems. DESI is well suited for hard, flat sample surfaces and not for soft, porous materials. It is tolerant to some surface structure or curvature. Height differences of 0.5–1 mm are acceptable without dramatic ion intensity losses; however, flat samples are best suited. Spatially resolved analysis can be typically performed from sample areas in the range of several millimeters to centimeters. Quantitative analysis, although in principle possible as shown, is difficult to implement for authentic consumer goods. Since only the oxidized species on the sample surface are

detectable with the method, no conclusion can be drawn as to the total metal content, as would be needed, for example, for lead and cadmium in jewelry. The concentration of oxidized species on the surface is influenced by many factors such as production, handling, and environmental conditions. As mentioned before the method's quantitative results can be best compared with migration or metal release studies. In this case, calibration standards would be needed from the same material as the sample (e.g. metal) with defined metal salt concentration (e.g. 10 $\mu\text{g}/\text{cm}^2$ nickel salt) on the surface. This could be achieved by spraying a solution on a metal target. Spatially resolved analysis is not necessary for the screening of consumer goods but could be of interest for valuable objects which are too large or too fragile for other techniques offering spatially resolved metal analysis, such as scanning electron microscopy, energy-dispersive X-ray analysis, secondary ion MS, or laser ablation inductively coupled plasma MS. No damage or change of the sample surface was observed after analysis with reactive DESI-MS. However, reanalysis of SPE frit surfaces showed a clear decrease in metal-EDTA ion intensity compared to the first analysis of the surface. No clogging of the DESI sprayer capillaries or sparkover were observed under normal measurement conditions.

Although the developed reactive DESI method has no direct advantages over conventional XRF for screening of consumer goods, it expands the portfolio of analytes accessible with DESI-MS. This is of particular interest for the development of versatile MS instrumentation for on-site screening of multiple key analyte classes most relevant in consumer goods.

5 | CONCLUSION

A reactive DESI method using EDTA as chelating agent was developed and employed for the qualitative analysis of heavy metals in consumer goods. The detection of the heavy metals lead, cadmium, and nickel was possible in eight out of nine authentic samples ranging from jewelry to tableware and toys. The quantitative performance and reproducibility of the method were determined and found to be comparable to those of other DESI-based methods. The LOD was 25 pmol/mm^3 for cadmium, 44 pmol/mm^3 for lead, and 279 pmol/mm^3 for nickel on SPE frits. In addition, lead was detected with the reactive DESI method from an authentic sample with a total lead content of 2.5 ppm. The method can be used for spatially resolved analysis with a resolution of about 200 μm as demonstrated for the print of a coffee cup. The method is also suited to analyze metal-containing pigments of paint in different media such as oil, egg tempera, and acrylic binder as shown by a proof-of-principle experiment.

AUTHOR CONTRIBUTIONS

Elena Maiworm: Investigation; formal analysis; methodology; data curation; validation. **Julius Wollmann:** Investigation; formal analysis; methodology; validation. **Tim Seiler:** Writing—original draft. **Michael Waletzko:** Investigation; methodology; formal analysis. **Sabine Schulz:**

Writing—original draft; conceptualization; funding acquisition; visualization; formal analysis; project administration; supervision.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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