Pb Correction Algorithms for Non-destructive Provenancing of Lead and Tin Glazed Slip Wares

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Abstract Lead and tin glazed pottery is frequently contaminated with Pb abundances even on the non-glazed surfaces of vessels and fragments. Elevated lead concentrations result in Pb specific matrix absorption and spectral interference effects on several discriminative trace elements - Ga, Rb and Y - which are important for fully non-destructive micro-chemical provenance based on portable x-ray fluorescence (pXRF) analysis. Empirical Lachance-Trail type correction algorithms have been developed by simulating increasing Pb surface abundances on fired clay samples with lead acetate sprayed on 4.0 μm polypropylene film. For paste surface layers with up to approximately 1 % w/w elemental lead concentrations, full compensation could be achieved, as demonstrated for a representative production waster assemblage of early modern lead glazed slip ware (Weser ware). Since the number of discriminative minor and trace elements in portable and stationary XRF of pottery is at the limit, the development of robust empirical correction algorithms for lead based matrix effects and spectral interferences and the validation of the applied quantification software, respectively, is essential.

Keywords pXRF Compositional Analysis, Spectral Interference Pb, Ga, Rb, Y, Calibration Spiked Clay Standards

1. Introduction

Among the many applied tasks of geochemical trace element analysis is provenance of lithic archaeological remains, like the attempt to elucidate the production region or even place of ancient pottery found in an archaeological context. The basic concept of compositional provenance is the expectation, that natural lithic raw material deposits exhibit a more or less unique trace element pattern, which can be used for back-tracing of artefacts having been exchanged or traded over long distance [1, 2]. In the case of ceramic produce potters may have used various local clays

over time, but may also have added a certain amount of nonplastic, coarse or fine-grained temper to modify the technological properties of the resulting wares. Thus there are two possible sources of trace elements contributing to the final pattern in the fired sherd, clay and temper and its respective precursor minerals [3].

There is a growing demand for fully non-destructive analysis of archaeological material, both for conservational reasons but also for increased sample throughput, with portable XRF spectrometers presently being the only suitable instruments for micro-chemical ceramic paste analysis. It is not so much the field applicability which gives preference to pXRF devices as compared to micro-XRF, particle-induced X-ray emission (PIXE) or micro-destructive laser ablation sampling, but the unrestricted access of the instrument window to study material of whatever size, and the larger "sample volume" which better accommodates the intrinsic heterogeneities of ceramic fabrics [4]. Since in non-destructive analysis the surface of the ceramic fragments cannot be rigorously cleaned from intentional as well as post-depositional modifications, particular care must be taken that the trace element composition of the paste is not distorted by any surficial modifications. In the case of salt and lead glazed pottery, glazed areas of fragments and vessels are precluded from non-destructive analysis. The glaze as such acts as a physical barrier for the element specific photons excited in the paste, with lead as a heavy element being a particularly potent photon absorber. However, in the case of lead glazed pottery even unglazed wall sides and biscuit fired dishes and bowls typically exhibit elevated Pb intensities, probably derived from lead volatilization during the firing process [5]. Diffusion of lead from the lead-alkali glaze towards the ceramic body during firing has also been hypothesized [6]. An additional source of surficial lead contamination of unglazed pottery may be acid leachates in production wasters, containing both glazed and unglazed wares, which are easily adsorbed to the surface of low-fired porous ceramics [7, 8]. As previously recognized [5] and further detailed below, surficial Pb contaminations strongly interfere with the analysis of the discriminative trace elements Ga, Rb and Y, and its accurate

quantification depends on empirical Pb correction algorithms, since more generalized fundamental parameter based quantifications seem to fall short. Furthermore Pb specific photon absorption ("Pb matrix absorption") needs to be corrected for any other discriminative elements like Ti, Fe, Sr, Zr and Nb.

Typical North European early modern slip wares, dishes and flat bowls with inside lead glazed slip decoration, are shown in Figure 1. The fragment in Figure 1b is a biscuit firing before lead glaze application from a workshop established around 1600 in Enkhuizen, The Netherlands, by a Dutch merchant, who intended to bypass the imports of prestigious Werra ware from the traditional German production region at the Werra River (several villages in the modern German states of Hesse, Thuringia and Lower Saxony) [9]. The unglazed outer wall and bottom parts of all fragments exhibit varying lead abundances.

2. Methods

A BRUKER Tracer III-SD portable XRF analyser with Rh tube placed in a benchtop stand has been employed. Per calibration sample 5 – 10 replicate analyses have been acquired, and 2 – 4 spots per ceramic fragment were analysed for 120 sec each at a tube power of 40 kV and 10.3 μ A with a 25 μ m Ti/ 300 μ m Al beam filter. The BRUKER software

S1PXRF 3.8.30 operated with PC trigger was used for signal acquisition. Background stripping and Bayes peak deconvolution of spectra was conducted with ARTAX 7.4.0.0 (BRUKER). For distance correction of concave sherds the resulting net counts were ratioed to the Rh $K\alpha_{1,2}$ peak (Rayleigh scatter of the Rh tube, [10]). For quantification the Rayleigh normalized net counts were converted into element mass fractions based on empirical calibration factors established with spiked fired clay samples (blank of a commercial clay, particle size 99.8 % <63 μ m, plus 4 concentrations each of Ti, Fe, Ga, Rb, Sr, Y, Zr and Nb, respectively, fired for 2 hrs. at 800-850 °C) [4]. For Pb spraying on Prolene 4.0 μ m film and Pb spiking, reagent grade lead (II) acetate trihydrate, $\geq 99\%$ (Sigma-Aldrich) has been used. Fe absorption/ enhancement as well as spectral interference of Rb $K\beta$ / Y $K\alpha$ and Y $K\beta$ / Nb $K\alpha$ [4] was corrected with empirical element specific Lachance-Trail algorithms [11]. Peak overlap of Sr $K\beta$ on Zr $K\alpha$ in the concentration range found in the pottery assemblages was properly corrected by the ARTAX software. Gross validation of the spiking curves was conducted with 12 geochemical reference materials (SARM 1, 41, 42, 44, 45, 48, 50, 52 and 69, South African Bureau of Standards, and CGL 002, 006 and 007, Mongolia Central Geological Laboratory). All concentration data are w/w % of the elements. For data processing Excel, R and ggobi were used.

Figure 1. Fragments of early modern slip wares - above decorated insides, below unglazed outsides. (a) 17th century Werra ware, probably from Hesse or Lower Saxony, Germany. (b) 17th century Werra ware, biscuit firing, waster sherd from Enkhuizen, The Netherlands. (c) 17th century Weser ware, waster sherd from Voelksen, Lower Saxony, Germany. (d) 18th century Rhenish lead glazed slip ware, waster sherd from Frechen/Cologne, Germany.

3. Results

3.1. Pb Matrix Absorption

In the photon energy range <40 keV Pb exhibits several L and M lines which differ in energy from 2.345 to 14.764 keV. The lower the energy of the line the more its fluorescence is absorbed by the clay matrix. To simulate surficial Pb (i), matrix/paste Pb (ii) and Pb glaze on the distal side (iii) fired clay samples have been analysed with placing a Prolene 4.0 μ m film sprayed with different lead acetate solutions between the instrument window and the sample (i), a set of fired clay samples spiked with lead acetate (ii), and a small lead weight has been placed on top of the measured sample (iii, sample

thickness 3 mm, Figures 2 and 3). The Pb M α peak having the lowest energy, is only visible upon Pb surface treatment. The Pb L α 1,2 peak is attenuated much stronger than the Pb L β 1,2 and the Pb L γ 1,2 peaks. In the analysed pottery assemblages the unglazed wall side always exhibited a higher Pb L α 1,2 than Pb L β 1,2 peak, indicating that surficial Pb contamination was the dominant source of Pb photon intensity in the XRF spectra.

Figure 2. Attenuation of Pb L and M shell photon energy depending on the information depth (Pb net counts ratioed to the Pb L β 1,2 peak)

Figure 3. Spectral overlay of blank fired clay (blue line) and blank fired clay with lead acetate sprayed on Prolene 4.0 μ m film (red line)

As shown in Figure 3 and Table 1 there is only modest photon absorption of the elements Ti, Fe, Sr, Zr and Nb by surficial Pb abundance, which could be corrected with Lachance-Traill type influence coefficients (graph only shown for Zr, Figure 4). The Pb La1,2 peak has been used for Pb absorption correction because it provides the best counting statistics and does not interfere with any other element of interest (any significant As abundance hidden under the Pb La1,2 peak would be recognized by its As Kb1 peak at 11.725 keV). The influence coefficients for Pb absorption are setting specific, but are valid over an extended range of concentrations of the effected elements (*i.e.* for the mass fraction range typically found in pottery). Conversion of surficial Pb intensities into w/w concentrations is semi-quantitative, since the Pb calibration like all other calibrations is based on homogenous elemental distribution in a fabric of infinite thickness. Surficial Pb intensities are thus given in arbitrary units (Pb net counts).

Figure 4. Correction of Zr net counts for surficial Pb absorption (lead acetate sprayed on Prolene film, Zr mass fraction of the clay blank 315 ± 6 ppm)

3.2. Pb Spectral Interference

By contrast the intensity peaks of Ga, Rb and Y are strongly impacted by Pb peak overlap, and the ARTAX software does not properly correct for these interferences (Figures 3, 5, 6 and 7). The Pb L1 peak fully overlaps the Ga Ka1,2 peak, and Ga mass fractions are strongly over reported with increasing surficial Pb abundances (Figure 5). The Y Ka1,2 peak is flanked by the Pb Ly1 and Pb Ly2 peak, and the Y mass fractions are overreported as well (Figure 6). The Rb Ka1,2 peak is least impacted, namely by a confluent shoulder of the Pb Lb2 peak (Figure 7). The Rb mass fractions are modestly underreported, probably due to unadapted background stripping.

Figure 5. Pb peak overlap correction for Ga. α strongly depends on the Ga concentration in the typical range of pottery (green zone, 15-50 ppm Ga)

Pb spectral interference could also be corrected with Lachance-Traill algorithms. The empirical Ga, Rb and Y influence coefficients cover both Pb absorption and Pb peak overlap. Unlike Pb absorption, the numerical values (α factors) of the Lachance-Traill type correction terms for spectral interference, however, are only valid for a narrow concentration range of the effected element. Particularly at low Ga and Y mass fractions and high Pb surface contamination the peak area ratios get

highly unfavourable, thus adding considerable uncertainty to the overall quantification of these two elements, which in clays and pottery are typically close to the detection limit of energy dispersive XRF.

Figure 6. Pb peak overlap correction for Y. α strongly depends on the Y concentration in the typical range of pottery (green zone, 15-50 ppm Y)

Figure 7. Pb peak overlap correction for Rb. α modestly depends on the Rb concentration in the typical range of pottery (green zone, 60-200 ppm Rb)

Table 1 summarizes the outcome of a successful Pb matrix absorption correction for Ti, Fe, Sr, Zr and Nb as well as for the combined absorption and spectral interference correction for Ga, Rb and Y, compared with the uncorrected quantification results.

Table 1. Effect of simulated Pb surface contamination on accuracy and precision with and without correction of Pb absorption and spectral interference

without Pb correction	Pb % *	Fe %	Ga %	Nb %	Rb %	Sr %	Ti %	Y %	Zr %
Surface Pb-0 (blank)	0.00	1.37	0.0026	0.0025	0.0145	0.0090	0.812	0.0040	0.0299
Surface Pb-1	0.01	1.43	0.0027	0.0025	0.0148	0.0092	0.828	0.0042	0.0309
Surface Pb-2	0.06	1.40	0.0031	0.0025	0.0144	0.0090	0.805	0.0041	0.0302
Surface Pb-3	0.25	1.39	0.0049	0.0024	0.0135	0.0089	0.759	0.0048	0.0298
Surface Pb-4	0.36	1.35	0.0060	0.0022	0.0132	0.0089	0.747	0.0052	0.0302
Surface Pb-5	0.69	1.22	0.0096	0.0022	0.0117	0.0084	0.607	0.0060	0.0278
Surface Pb-6	1.12	1.14	0.0138	0.0020	0.0108	0.0085	0.520	0.0072	0.0272
Mean	-	1.33	0.0061	0.0023	0.0133	0.0088	0.725	0.0051	0.0294
%RSD	-	8.15	68.22	8.86	11.23	3.47	16.12	23.13	4.65
with Pb correction	Pb % *	Fe %	Ga %	Nb %	Rb %	Sr %	Ti %	Y %	Zr %
Surface Pb-0 (blank)	0.00	1.37	0.0026	0.0025	0.0145	0.0090	0.814	0.0040	0.0299
Surface Pb-1	0.01	1.44	0.0026	0.0025	0.0148	0.0092	0.833	0.0041	0.0310
Surface Pb-2	0.06	1.42	0.0026	0.0025	0.0147	0.0091	0.829	0.0040	0.0304
Surface Pb-3	0.25	1.47	0.0026	0.0025	0.0145	0.0091	0.857	0.0041	0.0307
Surface Pb-4	0.36	1.46	0.0026	0.0024	0.0147	0.0092	0.886	0.0042	0.0315
Surface Pb-5	0.69	1.42	0.0027	0.0024	0.0144	0.0089	0.829	0.0040	0.0304
Surface Pb-6	1.12	1.44	0.0027	0.0023	0.0149	0.0093	0.831	0.0040	0.0312
Mean	-	1.43	0.0026	0.0025	0.0147	0.0091	0.840	0.0040	0.0307
%RSD	-	2.34	2.30	3.43	1.13	1.66	2.85	2.17	1.80

* Conversion of Pb surface net counts into Pb weight percent is semi-quantitative; ** Relative Standard Deviation in %

Figure 8. Bivariate scattergrams of element mass fractions with (red squares) and without Pb absorption and peak overlap correction (black crosses), respectively. Waster sherds ($n=250$) from a Weser ware workshop at Voelksen, Lower Saxony, Germany, 1600 - 1800

3.3. Pb Correction of Waster Material

The proper correction of Pb and any other matrix and spectral interference effects, is a matter of accuracy of the resulting mass fraction data. However, there is also a practical necessity to remedy such methodological inconsistencies, namely in order to achieve the intended purpose of ceramic provenancing, *i.e.* the distinction of different production centers. Due to the geochemical nature of the fabric, clay and temper, there is considerable compositional variation within the inventory of a localized production center (a reference group), but only modest differentiation between geographically distant sites [4]. Thus when many reference groups are plotted in bi- or trivariate trace element scattergrams, there is plenty of overlap in the periphery of the individual clusters. Apart from analytical

diligence it is therefore mandatory to avoid any methodologically caused scatter intensification which may further enlarge the apparent concentration range of discriminative trace elements in a particular reference group and thus artificially enhance cluster overlap.

In Figure 8 scattergrams of minor and trace elements determined in waster material from a single early modern pottery workshop in Lower Saxony, Germany, are displayed with (red squares) and without Pb absorption and spectral interference correction (black crosses). The waste material consisted of plain, unglazed earthenware, inside glazed utilitarian ware and inside slipped ware, predominantly dishes and bowls decorated with geometric and/or figurative motives (Weser ware [12], *cf* Figure 1c), which probably had a broad North-European distribution area to be identified in future provenance studies. Ti, Fe, Sr, Zr and Nb are impacted

by surficial Pb absorption only, and the effect of absorption correction is just a slight increase of the respective mass fraction values, as evidenced in the Zr/Nb scattergram (Figure 8a). Among the elements impacted by Pb peak overlap a slight increase of the Rb values can be recognized (Figure 8b), in line with the distorting effect of the Pb L β 2 shoulder on the background stripping of the Rb K α 1,2 peak. By contrast the Pb correction effect on the over reported Y and Ga concentrations (Figure 8c and d) is highly significant. The cluster density is strongly improved, and the resulting cluster shape is typical for production sites with a restricted number of geochemically closely related clay deposits. In the case of Ga the mean concentration of the Pb corrected assemblage is 19 ± 4 ppm, whereas the mean value of the uncorrected file amounts to 38 ± 28 ppm, with erroneous single values, depending on the extent of Pb contamination, of above 100 ppm.

4. Discussion

Islamic and Hispano-Moresque lead glazed pottery, Italian archaic and Renaissance majolica, French Saintonge slip ware, Dutch and German slip wares (Werra, Weser and Lower Rhenish decorated pottery) all had a broad distribution beyond their narrow production regions. The North European continental wares are found in archaeological contexts around the North Sea [12-14], and the South European produces in the circum-Mediterranean, but also on the British Isles [15,16]. Though the wares can be distinguished stylistically, similar produce, probably under stylistic influence, has been manufactured at different places (e.g. Werra ware, Figure 1 a, b), and its provenance cannot be determined by mere art historian stylistic characterization. Archaeologists therefore depend on compositional analysis if they want to hypothesize the production origins and trade routes.

At present micro and portable XRF instruments are the only devices for true non-destructive compositional analysis of ceramics. Thereby the method is still considered as experimental, and its accuracy is frequently questioned, particularly for poor factory calibrations of the portable instruments and lack of validation with certified reference materials [17-21]. Proper calibration is, however, possible with matrix matched reference materials [21] and with spiked fired clay samples in particular [4]. Spiked concentration series are also required for establishing range specific algorithms for correction of spectral interferences, namely of Rb/Y, Y/Nb and Sr/Zr peak overlap. Empirical Pb absorption and interference correction is thus just an extension of the mandatory calibration and validation effort for quantitative trace element determination of a particular kind of sample material.

5. Conclusions

For non-destructive compositional analysis of pottery with

lead contaminated surface, empirical correction algorithms have been established which compensate for Pb absorption as well as Pb spectral interference of Ga, Rb and Y. Applying such correction terms is a prerequisite for accurate quantification of minor and trace elements in lead contaminated ceramic fabrics, and its utility for cluster shape improvement has been demonstrated with waster material of an exemplary early modern pottery production workshop. Whether Pb absorption and interference correction is necessary and to what extent, is a matter of sophistication of the applied deconvolution algorithms, but without proper check and validation of the quantification software used with the spectrometers erroneous results are bound to occur.

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