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ABSTRACT

Falling costs, smaller sizes and increasingly userfriendly interfaces have led to the wide use of handheld portable x-ray fluorescence instruments (HHpXRF) in the analyses of cultural heritage objects. Methodological considerations on the validity of results derived from HHpXRF have led to debates in conservation and archaeological literature. Relatively little attention has been paid to the applicability of HHpXRF to the characterisation of archaeological copper alloys. This paper evaluates the use of Bruker AXS Tracer III-SD on a range of certified copper alloys which were selected based on their occurrence in antiquity. Alloys were then electrochemically corroded and analysed to examine the impact of corrosion layers on HHpXRF data. Qualitative and quantitative data processing methods are compared and the impact of sourceto-sample distance on the HHpXRF results is examined. The implications and relevance of data accuracy are discussed with regard to archaeological interpretation and uses in conservation.

INTRODUCTION

The increasing affordability of handheld portable x-ray fluorescence spectrometers (pXRF or HHpXRF) has led to widespread growth in their application to cultural heritage objects. Advantages of HHpXRF include in-situ analyses on museum objects or in the field, with fast and easy data collection. This has not been without controversy, with debates on a range of issues from reproducibility, accuracy and methodological challenges to the validity of the data produced (Shackley 2010, Frahm 2013, Frahm and Doonan 2013, Speakman and Shackley 2013). Several works focus on quantitative analysis of homogenous materials such as obsidian (Nazaroff et al. 2010, Millhauser et al. 2011), qualitative assessment of biocides on museum objects (Podsiki 2009, Charola and Koestler 2010) and spatial geochemical analysis on archaeological sites (Davis et al. 2012). There has been little focus on heterogeneous materials such as corroded nonferrous metals. This paper offers an assessment of the applicability of the Bruker AXS Tracer III-SD HHpXRF to non-destructive analyses of archaeological copper alloys with focus on the characterisation of bulk alloy compositions, the effects of corrosion, tinning and sample geometry.

BACKGROUND

Characterisation of bulk alloy composition of archaeological copper alloys is crucial in investigating innovation and technological changes in past communities. Identification of plating methods furthers understanding of past technologies and informs conservation strategies. Although bench-top XRF is readily employed (Dungworth 1997, Bayley and Butcher 2004) and the physicochemical matrix effects are understood, little research focuses on challenges presented by HHpXRF employed on the surface of archaeological copper alloys. Interlaboratory assessment of calibrated XRF results has demonstrated the erroneous impact calibrations can have on the data (Heginbotham et al. 2011). Qualitative analyses using the ratio of the fluorescent peak intensities of selected elements (Shalev et al. 2006) as an indication of mass (Shilstein and Shalev 2011), have been successfully used for certain applications, but discarded for others (Shackley 2010). Alternatively, net peak areas (NPA), which can be produced before compositional calibrations, could be useful for a qualitative assessment of elemental ratios in alloys.

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TESTING THE APPLICABILITY OF HANDHELD PORTABLE XRF TO THE CHARACTERISATION OF ARCHAEOLOGICAL COPPER ALLOYS The fluorescence signal derives from about 0.1 mm depth of a copper alloy; thus, analyses can be misleading in the presence of corrosion (Dungworth 1997). This problem is often overcome by removing surface corrosion or samples for analyses (ibid.). Cleaning an area for HHpXRF analyses (c. 10 mm diameter) jeopardises the object's integrity and aesthetics. Corrosion of low tin-bronzes results in tin enrichment (Robbiola et al. 1998) that could reach compositions similar to tinning remains (Manti 2012). Tinning of bronzes forms a layered surface composed predominantly of metallic tin and η -Cu₆Sn₅ (61wt%Sn) and depending on the technique employed or use of object ϵ -CuSn₃ (37.74–39.50 wt%Sn) and/or δ -Cu₄₁Sn₁₁ (33.38 wt%Sn) (Manti and Watkinson 2010). When metallic tin or the η -Cu₆Sn₅ survives under corrosion deposits, surface HHpXRF should effectively detect higher tin counts indicative of tinning. Surface compositional data could be misleading where only sparse evidence of tinning remains. A better understanding of the impact of corrosion on the fluorescence signal is necessary.

Detection efficiency depends on source-to-sample distance due to the inverse square law. When analysing complete archaeological objects, the geometry of the object can restrict good contact with the spectrometer's window. The greater the distance of the object to the window, the less accurate/precise the results due to signal attenuation and changes in scattering angles, producing higher backgrounds and systematically lower fluorescence line intensities. Solutions to this problem include the use of fundamental parameter methods (Bos and Vrielink 1998) and applied corrections via normalisation of the measured intensity to flat reference samples (Potts et al. 1997). More work is required to understand the significance of these phenomena with regard to interpretation of the data. Understanding the implications and relevance of bulk analysis data accuracy is important given the increasing role HHpXRF can play in the ID of objects (Besly 2013 for an example) under the Treasure Act in England and Wales (DCMS 2002).

METHODOLOGY

Materials and methods

The performance of HHpXRF was evaluated based on analyses of certified copper alloys, six from MBH Analytical Ltd and five from the IMMACO project selected to meet ancient alloy compositions (Wadsak et al. 2000, Beldjoudi et al. 2001) (Tables 1–2). These include a quaternary bronze (A), brass (B), arsenical copper (C), leaded tin bronze (D) and low-tin bronze (E), with As, Pb, Sn and Zn certified values valid for an analysis spot diameter of 5 mm (Ingelbrecht et al. 2001). IMMACO compositions are typical of copper alloys used from the Bronze Age to the Roman period (Beldjoudi et al. 2001) and the MBH alloys are similar to early medieval alloys found in Europe (Mortimer 1991, Blades 1995). All analysed alloy tokens are infinitely thick in terms of the analytical depth of the x-ray beam.

The IMMACO metals were electrochemically corroded to investigate the impact of corrosion on the HHpXRF data. The process was undertaken in two stages, following Constantinides et al. (2002). Samples were degreased with acetone, half immersed in individual beakers held by crocodile clips, with a platinum-niobium coated solid copper wire rod acting as a cathode

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A basic examination of corroded alloys was conducted to confirm the nature of the corrosion layers. X-ray diffraction (XRD) analyses used an XPERT-PRO PAN analytical diffractometer. Flat samples were analysed in situ on a fixed stage with divergent beam footprint of 200 mm² for 15 sec/step (7-100°20) acquisition time. Data was analysed with X'Pert HighScore V2.1.2 and PDF-02 database. Samples were examined using scanning electron microscopy (SEM) with backscattered electron imaging (BSE). Compositional analysis employed a CamScan 2040 SEM (20 kV) with an Oxford Link Pentafet 5518 dispersive x-ray spectrometer (ATW2 window) and INCA software using no. 4629, Micro-Analysis Consultants Ltd standards for system calibration.

HHpXRF data acquisition and processing

Analyses used a Bruker AXS Tracer III-SD portable XRF equipped with a rhodium tube and silicon drift detector (SDD) and a 10×8 mm ellipse spot size as determined by exposure to x-ray film. The metal tokens were positioned directly on the detector window and analyses were undertaken in a Bruker bench-top stand. IMMACO alloys A and E (both uncorroded and corroded) were used to determine changes in the quality of the data due to increasing sample-to-source distance. Each token was positioned in contact to the detector window and then raised by 2 mm between readings to a maximum 12 mm.

Data acquisition was conducted using 40KV voltage and 9.6 μ A current with a 25 μ m titanium/300 μ m aluminium filter and 100 seconds acquisition time, using Bruker XRayOps v.1.2.15. This set-up allows for the effective excitation of higher Z elements. Ten analyses were acquired from each metal, each from a different area, except corroded IMMACO and tinned alloys due to their restricted surface area. This permitted assessment of alloy homogeneity and enabled statistical evaluation of the measurements.

Spectra were visually examined individually for the presence or absence of elements and shift in eV using the Bruker S1PXRF v.3.8.30 software. Practical experience has shown that shift in eV per channel is possible due to the silicon detector drift. The Bruker ARTAX v.7.3.5 software was used for qualitative data analysis with NPA for all elements present calculated. ARTAX uses an automated process, which involves the deconvolution and evaluation of the spectra, including background and escape corrections. Data were then processed using S1CalProcess v.2.2.32 with empirical calibrations to produce wt% elemental compositions. Empirical calibrations were constructed using analyses on the uncorroded MBH and IMMACO alloys. Data were normalised in S1CalProcess using the region of interest (ROI). Appropriate slope and background corrections were made for

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The NPA and wt% concentrations from each analysed sample were averaged (mean, n=10) and the standard deviation (SD) and coefficient of variation (C_v) calculated. The limit of determination of a method (LDM) was calculated to offer information on repeatability of results within 95.4% confidence level (Rousseau 2001).

RESULTS AND DISCUSSION

Examination of electrochemically corroded alloys

Electrochemical corrosion showed good agreement with patinas produced on the IMMACO metals elsewhere (Constantinides et al. 2002). XRD on the corroded surfaces showed the presence of malachite (PDF 00-041-1390), cuprite (PDF 00-078-2076) and small amounts of paratacamite (PDF 00-015-0694) on all samples. Nantokite (PDF 00-077-2383) is predominately found on IMMACO B (brass) in addition to ZnS (PDF 01-071-4763) and ZnO (PDF 00-005-0664). A blue crystalline compound on IMMACO D is composed of sodium carbonate (PDF 01-078-007) and sodium lead carbonate (PDF 00-037-0501). SEM-BSE imaging (Figure 1) shows corrosion layers on all samples ranging between c. 10–150 μ m depending on uniformity and pitting. The IMMACO A and E exhibit similar corrosion with a well-defined corrosion layer that marks the original



Figure 1

BSE images of corroded IMMACO metals in polished sections. Images taken at x500 magnification; detail on IMMACO C at x1000 magnification

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HHPXRF RESULTS

Quantitative results - Empirical calibrations

Tables 1 and 2 present results of corroded and uncorroded reference alloys. MBH alloys were analysed as unknowns to check the calibration quality (Table 1, Figure 2). The same alloys were used for the calibration, constraining calculation of the global uncertainty. Results show good reproducibility (SD and LDM) and accuracy for major elements (Cu, Sn, Zn, Pb), which is decreased for lower concentrations of Pb (32XSN6) and low As content in all alloys.

Reproducibility and accuracy are slightly decreased for the IMMACO metals (Table 2, Figure 3), but mean concentrations lie within certified uncertainty for low As concentrations (IMMACO A, B, D, E), Pb and Sn (IMMACO D). 32XLB10 is very similar to IMMACO D used for calibration. Pb and Sn are slightly higher for IMMACO A, demonstrating the need for alloys similar in the composition used for empirical calibrations. Some variation of Pb and Sn in leaded bronzes may be due to inhomogeneity and a larger analysis spot size used compared to certification.



Figure 2

Empirically calibrated wt% analyses of the MBH alloys

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Figure 3

Empirically calibrated wt% analyses of the IMMACO alloys before and after corrosion. Uncertainty on given values from Ingelbrecht et al. (2001)

Analytical reproducibility further decreased after corrosion of IMMACO metals. The impact of corrosion is evident with the drastic reduction of Zn concentration in brass (B) due to dezincification, loss of As in arsenical copper (C) and a relative increase of Sn in alloys containing tin due to surface enrichment. Not unexpectedly the results show that the corrosion layer can affect accuracy of surface XRF measurements.

Qualitative results – NPA

NPA results (Table 3, Figure 4) of IMMACO samples show good reproducibility for copper, tin and zinc, but significant spread for arsenic and lead. Precision is affected by corrosion, with evidence for the increase of tin (IMMACOA, D) and decrease of copper, zinc and arsenic (A, B, C), similar to the empirically calibrated results. Preliminary analyses of HHpXRF results from corroded and uncorroded tinned-copper samples show (Figure 5) increase of tin fluorescence line intensity (S15, S19) due to tinning which lies close to the intensity of the low-tin bronze (c. 10 wt%) substrate (B7). S1 shows unexpectedly lower intensity likely due to the small tinned surface area on the copper sample. The tinned bronze (B7) exhibits the highest tin intensity due to the additional tin concentration from the bronze substrate, indicating that a large portion of the signal derives from the substrate. If a fine patchy layer of tinning remains on archaeological bronzes under corrosion deposits, an increase of tin concentration could be similar to that from corrosion tin-enrichment. More work on archaeological objects is necessary to understand how corrosion would affect identification of tinning.



Cu Ka Zn Ka 7.00E+06 1.40F+06 4.00E+06 8.00E+05 1.00E+00 0.00E+00 D С D в С F в Е Ν Δ Δ e Sn Ka Pb L t 1.80E+05 4.00F+05 Ρ е а 2.00E+05 8.00E+04 k А 0.00E+00 r 0.00E+00 В С D С D A Ε A В Е е а As Ka Sb Ka S 3.00E+05 1.00E+04 1.50E+05 5.00E+03 0.00E+00 0.00E+00 в С Е в С D Α D А F Uncorroded Corroded

Figure 5

Corroded and uncorroded tinned copper (S1, S15, S19) and bronze (B7), showing spectra of raw counts on a logarithmic scale



NPA HHpXRF analyses of the IMMACO alloys before and after corrosion

Source-to-sample distance

When testing the impact of source-to-sample distance, results show a systematic decrease in intensities (Figure 6) as a consequence of the inverse square law. Higher Z elements (Sn, Pb) appear over-represented relatively to lower Z elements (Cu, Zn) at greater distance, due to differences in x-ray absorption coefficients. This is amplified in the presence of Sn-rich corrosion layers, likely due to changes in the depth from which fluorescence derives on the surface of the sample. This effect intensifies after c. 5-mm distance indicating the importance of good sample/window contact for accurate analyses.

DISCUSSION

Plotting calibrated Cu-Zn-Sn values and NPA in a ternary diagram (Figure 7) allows assessment of the impact of corrosion and processing method on data interpretation and primary descriptive alloy classification (i.e. bronze or brass). Empirically calibrated data lay closer to the given compositions of uncorroded IMMACO alloys compared to the NPA values. The impact of corrosion is evident with a decrease of Zn in brass (IMMACO B) and a relative increase of Sn in IMMACO A, E and D for both data processing types. Although data processed as NPA deviate from given compositions in the plot, they are within the broader alloy classification regions in the Cu-Zn-Sn diagram often used in archaeometry (Dungworth 1997). Data processing such as NPA can produce useful qualitative data to facilitate fast screening of a large number of finds where an understanding of bulk composition is sought.

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Figure 6

IMMACO A and E. Line charts showing % reductions in raw fluorescence counts for increasing sourceto-sample distance and bar charts showing normalised ratios of NPA for CuK α , ZnK α , SnK α , PbL α



Figure 7

Detail of Cu-Zn-Sn ternary diagram showing given values, quantitative and qualitative results on uncorroded and corroded IMMACO alloys

CONCLUSION

A simple methodology has been used to assess the accuracy and precision of the net peak area results for major elements on a range of corroded and uncorroded certified alloys compared to empirically calibrated compositions. Results showed that HHpXRF is not capable of producing highly accurate quantitative data on corroded surfaces, due to object

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Table 1

Given and empirically calibrated measured analyses of the MBH alloys (wt%). Empirically calibrated measured data (Cal. Measured), standard deviation (SD), coefficient of variation (C_v) and limit of determination of a method (LDM) are presented

Sample & Description	Fe K $lpha$	Co K α	Ni Ka	Cu K α	<mark>Zn K</mark> α	As K $lpha$	Bi Lα	Pb Lβ	Ag Ka	Sn Kα	Sb K α
31X B5											
Given values	0.06	0.01	0.01	76.22	23.60	0.01	0.01			0.05	0.01
Measured Mean (n=10)	0.05	0.04	0.02	76.63	23.45	0.05	0.03			0.25	n.d.
SD	0.003	0.004	0.002	0.01	0.02	0.002	0.001			0.003	
C _v	0.05	0.11	0.09	0.00	0.00	0.03	0.02			0.01	
LDM) (<u>+</u>)	0.005	0.01	0.004	0.02	0.03	0.003	0.001			0.01	
32X LB10											
Given values	0.01	0.05	0.69	77.98	0.57		0.06	11.74		8.16	0.59
Measured M,	0.04	0.04	0.69	77.58	0.32		0.02	11.44		8.39	0.58
SD	0.003	0.004	0.01	0.13	0.01		0.005	0.10		0.04	0.02
C _v	0.06	0.08	0.01	0.002	0.02		0.30	0.01		0.01	0.03
LDM (<u>+</u>)	0.01	0.01	0.01	0.26	0.02		0.01	0.20		0.09	0.03
32X PB10											
Given values	0.01		0.05	87.85	0.05	0.01	0.01	0.07		11.87	0.02
Measured M,	0.05		0.05	87.45	0.01	0.05	0.04	0.09		12.11	0.03
SD	0.002		0.001	0.04	0.01	0.002	0.001	0.01		0.04	0.01
C _v	0.05		0.03	0.000	0.47	0.04	0.02	0.08		0.003	0.27
LDM (<u>+</u>)	0.004		0.003	0.08	0.01	0.00	0.00	0.01		0.08	0.01
32x SN6											
Given values	0.10	0.66	0.20	86.39	1.17	0.77	0.16	1.56	1.16	7.31	0.32
Measured M,	0.07	0.66	0.24	86.32	0.95	0.95	0.14	2.78	1.15	7.44	0.34
SD	0.002	0.01	0.003	0.03	0.02	0.01	0.004	0.04	0.01	0.03	0.01
C,	0.03	0.01	0.01	0.000	0.02	0.01	0.03	0.01	0.01	0.004	0.02
LDM (<u>+</u>)	0.004	0.01	0.01	0.05	0.03	0.02	0.01	0.07	0.01	0.05	0.01
33X GM29											
Given values	0.01		0.03	89.36	4.23			0.05		6.12	
Measured M,	0.04		0.03	88.80	3.91			n.d.		5.68	
SD	0.002		0.002	0.08	0.01					0.09	
C,	0.05		0.07	0.001	0.003					0.02	
LDM (<u>+</u>)	0.004		0.005	0.16	0.02					0.18	
74X CA7											
Given values				0.33		0.01	0.01	0.10	4.21	95.26	0.01
Measured M,				0.33		n.d.	0.23	0.10	4.23	95.41	0.03
SD				0.05			0.005	0.01	0.02	0.17	0.04
C _v				0.14			0.02	0.09	0.005	0.002	1.42
LDM (<u>+</u>)				0.09			0.49	0.02	0.04	0.34	0.07
n.d. not detected											

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Table 2

Given and empirically calibrated analyses (Cal. Measured) of IMMACO alloys before and after corrosion (wt%). Standard deviation (SD), coefficient of variation (C_v) and limit of determination of a method (LDM) are presented

Sample & Description	Mn Kα	Fe K α	Ni Ka	CuKlpha	$Zn K\alpha$	As K α	Pb Lβ	Sn K α	Sb K α
IMMACO A									
Given values	0.2	0.2	0.1	76.5	6	0.2	9	7	0.5
Measured Mean (n=10)	0.2	0.2	0.1	77.2	6.1	0.1	10.5	7.1	0.5
SD	0.01	0.01	0.03	0.46	0.29	0.16	0.52	0.44	0.03
C _v	0.04	0.03	0.39	0.01	0.05	1.9	0.05	0.06	0.06
LDM (<u>+</u>)	0.01	0.01	0.05	0.93	0.58	0.31	1.04	0.89	0.05
Corroded Measured Mean (n=10)	0.2	0.2	0.1	79.8	6.9	n.d.	7.7	7.5	0.6
Corroded SD	0.08	0.06	0.07	1.81	2.34		0.06	0.46	0.03
Corroded C _v	0.41	0.27	1.06	0.02	0.34		0.01	0.06	0.05
Corroded LDM (<u>+</u>)	0.01	0.02	0.01	1.4	1.07		0.69	1.09	0.05
IMMACO B									
Given values	0.4	0.5	0.2	81.1	15	0.1	0.4	2	
Measured M.	0.4	0.5	0.2	79.6	15.3	0.1	0.7	1.9	
SD	0.01	0.01	0.01	0.11	0.15	0.01	0.04	0.04	
C,	0.02	0.03	0.04	0	0.01	0.08	0.06	0.02	
LDM (<u>+</u>)	0.018	0.027	0.02	0.23	0.31	0.02	0.08	0.09	
Corroded M. M.	0.6	0.6	0.1	82	12.3	0.1	0.9	2.6	
Corroded SD	0.03	0.02	0.02	0.82	0.97	0.01	0.06	0.14	
Corroded C	0.05	0.03	0.26	0.01	0.08	0.1	0.07	0.06	
Corroded LDM (<u>+</u>)	0.06	0.03	0.05	1.64	1.95	0.03	0.12	0.29	
IMMACO C						L			L
Given values	0.2	0.2		93.4	0.06	5	0.2	0.2	0.5
Measured M.	0.2	0.2		93.6	n.d.	4.9	n.d.	0.4	0.4
SD	0.01	0.02		0.41		0.42		0.01	0.01
C,	0.06	0.11		0.004		0.09		0.01	0.03
LDM (<u>+</u>)	0.02	0.05		0.82		0.85		0.01	0.03
Corroded M. M.	0.2	0.2		95.4	n.d.	3.3	0.1	n.d.	0.6
Corroded SD	0.01	0.02		0.36		0.31	0.04		0.02
Corroded C	0.04	0.09		0.004		0.09	0.34		0.04
Corroded LDM (<u>+</u>)	0.02	0.04		0.72		0.62	0.09		0.05
IMMACO D	1			1			1		
Given values	0.1	0.1	0.3	78.8	0.1	0.3	10	10	0.3
Measured M.	0.11	0.1	0.38	78.78	0.29	0.31	9.39	9.89	0.24
SD	0.01	0.01	0.06	0.45	0.06	0.07	0.15	0.22	0.06
C,	0.05	0.14	0.14	0.01	0.2	0.22	0.02	0.02	0.23
LDM (<u>+</u>)	0.01	0.03	0.11	0.91	0.12	0.14	0.31	0.45	0.11
Corroded M. M.	0.1	0.1	0.4	76.1	0.4	0.1	10	11.1	0.4
Corroded SD	0.01	0.03	0.1	1.25	0.35	0.23	0.63	0.47	0.05
Corroded C	0.06	0.21	0.27	0.02	0.87	1.98	0.06	0.04	0.14
Corroded LDM (<u>+</u>)	0.01	0.05	0.2	2.49	0.7	0.47	1.27	0.93	0.1
IMMACO E				1			1		
Given values	0.3	0.3	0.5	90.2	0.1	0.2	0.2	7	0.7
Measured M.	0.29	0.33	0.49	89.95	0.62	0.22	0.38	6.83	0.72
SD	0.012	0.022	0.008	0.097	0.022	0.01	0.017	0.09	0.016
C,	0.04	0.07	0.02	0.001	0.04	0.04	0.04	0.01	0.02
 LDM (<u>+</u>)	0.02	0.04	0.02	0.19	0.04	0.02	0.03	0.18	0.03
Corroded M. M.	0.3	0.4	0.5	89.9	n.d.	0.2	0.3	7.5	0.8
Corroded SD	0.06	0.05	0.11	1.04		0.03	0.07	0.6	0.06
Corroded C	0.21	0.14	0.22	0.01		0.16	0.22	0.08	0.07
Corroded LDM (<u>+</u>)	0.13	0.1	0.21	2.08		0.06	0.14	1.2	0.12

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TESTING THE APPLICABILITY OF HANDHELD PORTABLE XRF TO THE CHARACTERISATION OF ARCHAEOLOGICAL COPPER ALLOYS Table 3

HHpXRF NPA results of IMMACO alloys before and after corrosion. Standard deviation (SD), coefficient of variation (C,) and limit of determination of a method (LDM) are presented

Sample & Description	${\rm Mn}{\rm K}\alpha$	Fe Ka	Ni Ka	Cu Ka	Zn Klpha	As K α	Pb L α	Sn K α	Sb K α
IMMACO A									
Measured Mean (n=10)	5268	10530	9075	4403332	524931	11586	156270	102880	5214
SD	324	342	456	66666	26648	2541	12400	1336	117
C _v	0.06	0.03	0.05	0.02	0.05	0.22	0.08	0.01	0.02
LDM (<u>+</u>)	648	685	912	133332	53297	5082	24800	2671	234
Corroded Measured Mean (n=10)	6294	8981	8035	4186419	438179	4045	73560	113163	5630
Corroded SD	686	320	482	59482	10579	414	3813	1480	219
Corroded C _v	0.11	0.04	0.06	0.01	0.02	0.10	0.05	0.01	0.04
Corroded LDM (<u>+</u>)	1372	641	964	118964	21157	828	7625	2960	438
ІММАСО В									
Measured M.	12956	30466	14914	4834170	1256514	2807	9643	31047	
SD	792	567	317	61163	19956	506	407	666	
C,	0.06	0.02	0.02	0.01	0.02	0.18	0.04	0.02	
LDM (<u>+</u>)	1583	1134	635	122327	39912	1012	815	1333	
Corroded M. M.	15196	36146	11540	4730744	1016898	2815	10331	33831	
Corroded SD	927	1817	333	182065	23670	339	654	1731	
Corroded C	0.06	0.05	0.03	0.04	0.02	0.12	0.06	0.05	
Corroded LDM (<u>+</u>)	1657	3252	595	325780	41863	597	1162	3105	
IMMACO C		1					1		
Measured M.	6225	12281		5879435	n.d.	240729	8076	3646	6255
SD	963	1100		85142		21190	1282	156	291
C _v	0.15	0.09		0.01		0.09	0.16	0.04	0.05
LDM (<u>+</u>)	1926	2201		170285		42381	2565	312	582
Corroded M. M.	6751	13592		5558775	n.d.		9326	3961	5932
Corroded SD	1009	870		164801		11377	1220	138	150
Corroded C _v	0.15	0.06		0.03		0.08	0.13	0.03	0.03
Corroded LDM (<u>+</u>)	2018	1740		329602		22754	2440	276	299
IMMACO D									
Measured M.	1254	3901	18172	4362832	33055	18718	268101	137945	2862
SD	296	212	322	80094	2121	2415	35092	2818	150
C _v	0.24	0.05	0.02	0.02	0.06	0.13	0.13	0.02	0.05
LDM (<u>+</u>)	592	424	644	160188	4242	4830	70184	5637	300
Corroded M. M.	1749	4873	18123	3806500	36330	17624	251577	155680	3281
Corroded SD	178	527	841	143712	2189	2346	17784	7629	152
Corroded C _v	0.10	0.11	0.05	0.04	0.06	0.13	0.07	0.05	0.05
Corroded LDM (<u>+</u>)	355	1054	1681	287424	4377	4692	35568	15258	400
IMMACO E									
Measured M.	8854	16140	28490	5082641	38244	7111	6352	108087	7818
SD	1057	527	562	59263	1774	365	259	1858	237
C _v	0.12	0.03	0.02	0.01	0.05	0.05	0.04	0.02	0.03
LDM (<u>+</u>)	2114	1054	1124	118526	3548	731	518	3717	475
Corroded M. M.	10670	14390	24962	4680045	38171	3653	4905	106394	7427
Corroded SD	1017	3433	4222	84186	5287	989	1053	10467	647
Corroded C _v	0.10	0.24	0.17	0.02	0.14	0.27	0.21	0.10	0.09
Corroded LDM (<u>+</u>)	6867	2035	1977	8444	168372	10575	2107	20934	1294

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