



Introducing “Full Scan” Glow Discharge Mass Spectrometry Analysis of Iron Oxides for Provenience Studies of Ochre Pigments

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Introduction

Provenience, or “sourcing”, studies of ochre pigments have proliferated since the mid-2000s and have become an accepted part of the archaeological sciences. Almost all such studies rely on elemental compositional data and multivariate statistical analysis to distinguish between geological sources of ochre and to assign unknown archaeological pigments to their origin. The instrumental techniques employed to generate these compositional data sets are diverse; among the most prominent are SEM-EDS, EPMA, XRF, NAA, and various forms of ICP-MS.¹ The method development study reported here represents the first application of Glow Discharge Mass Spectrometry (GDMS) to iron-bearing oxide reference materials using an oxide-specific set of relative sensitivity factors (RSF). With further development, especially analysis of geological samples of ochre that have previously been characterized, GDMS will be well-positioned to complement or replace the techniques noted above in the provenience analysis of ochres.

Diverse Examples of Natural Ochres



Figure 1.
A: Massive specular hematite
B: Martite habit of hematite
C: Ochreous yellow clay weathered from mica
D: Red and yellow ochreous shale
E: Ochreous red clay from igneous rock hydrothermally weathered

Glow Discharge Mass Spectrometry (GDMS)

GDMS is a solid sampling technique able to perform fast, reliable analysis of minor and trace elements down to sub-ppm levels. GDMS combines a glow discharge source with a high-resolution magnetic sector mass spectrometer, providing excellent sensitivity and mass resolution. The vast majority of commercially available GDMS instruments utilize a direct current (DC) source. Samples analyzed using DC current are introduced to the cell as the cathode. Nonconductive samples, such as the mixed oxides studied here, may be analyzed using binders or working electrodes to support the plasma.

EAG Laboratories has recently developed a generalized mixed oxide RSF set to enable more accurate analysis of nonconductive oxide materials on a tantalum (Ta) holding electrode.² There are two geometries samples can be analyzed in: flat and axial. The flat geometry allows for near-surface analysis, depth profiling, and analyzing thick films. The sampling orifice is ~10 mm in diameter. The axial geometry is ideal for conductive pins 22 mm long and 2 mm wide, powders, and small chunks. While the axial geometry lacks spatial resolution, it generally provides higher signal than the flat geometry.

During discharge, the sample is bombarded with positive ions from the argon plasma. Consequently, the cathode releases neutral atoms which diffuse into the plasma and get ionized (Figure 2). Ion beam intensities of all analytes are then measured using a combination of analog and digital detectors and evaluated in reference to a matrix element or normalized to multiple matrix elements. These ion beam ratios are converted to mass fractions using the RSFs which are developed through long term analysis of reference materials.² RSF values account for the different elemental ion yields in the plasma.

GDMS, when used as a standardless technique with generalized calibration factors, may be biased to within a factor of two relative to true concentrations. For provenience studies, this is no hindrance because the multivariate statistics involved rely on ratio relationships between element concentrations to distinguish among sources.

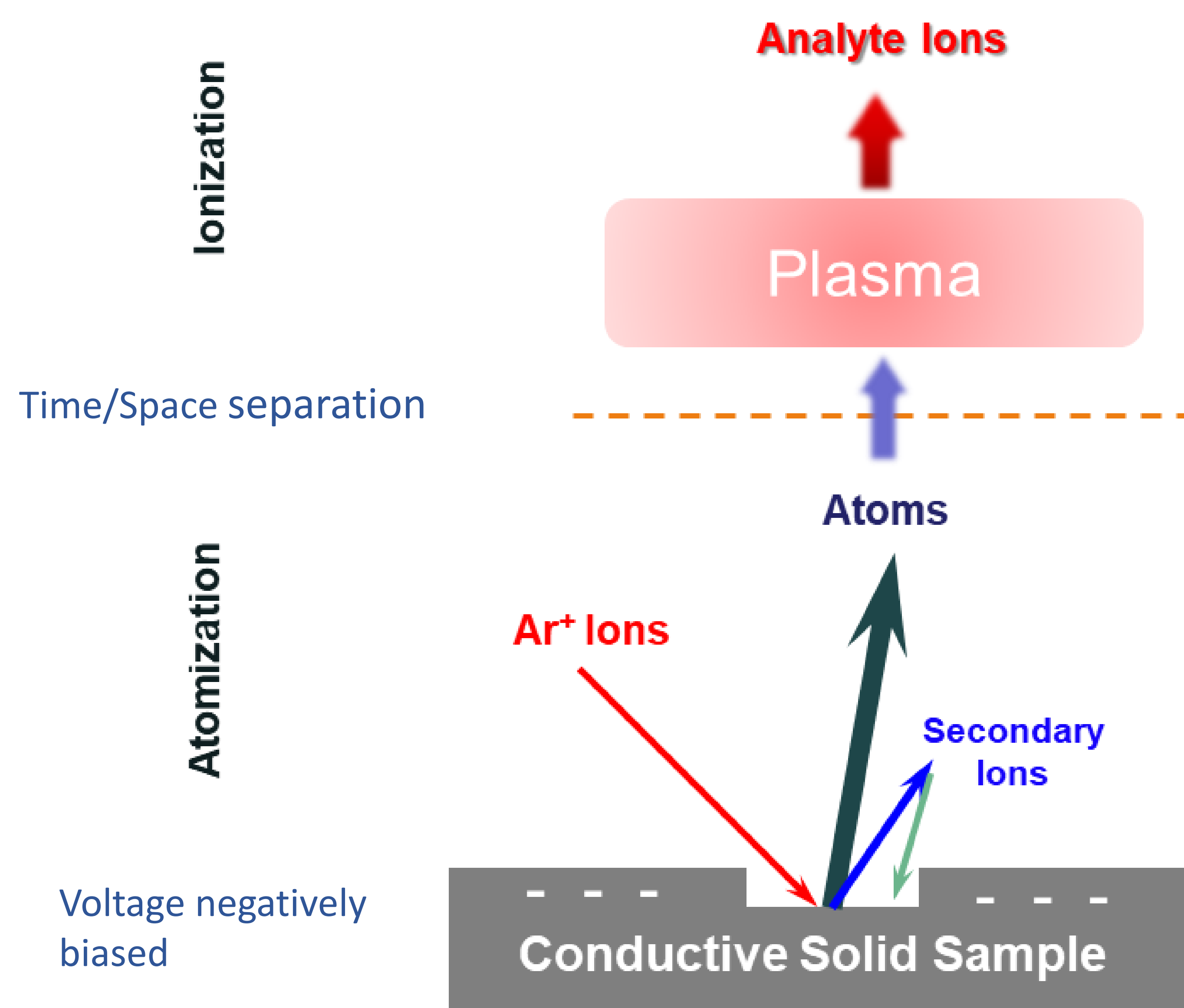


Figure 2. Schematic of glow discharge analysis of a conductive sample.

Methods

Five certified reference materials: NRC IOC-1 (65.66 wt% Fe), NIST SRM 692 (59.61 wt% Fe), USGS BCR-2 (9.63 wt% Fe), NIST SRM 679 (9.05 wt% Fe), and OREAS 25b (8.53 wt% Fe) were analyzed using an Ametek Nu Instruments Astrum ES with co-axial GD cell (Astrum GDMS). These CRMs were selected to represent some of the diversity of materials that may be considered ochre or precursors that form ochre by weathering. Approximately 10 mg of powder for each reference material were loaded to a chemically cleaned (1:1 HNO₃:HF solution) Ta holding electrode (Figure 3) for analysis. The samples were analyzed at 3.0 mA fixed current and 1000 volts, with argon flow adjusted to achieve the desired voltage. The samples were measured in triplicate across multiple days to account for the uncertainty caused by any variation in sample preparation and instrument conditions from day to day.

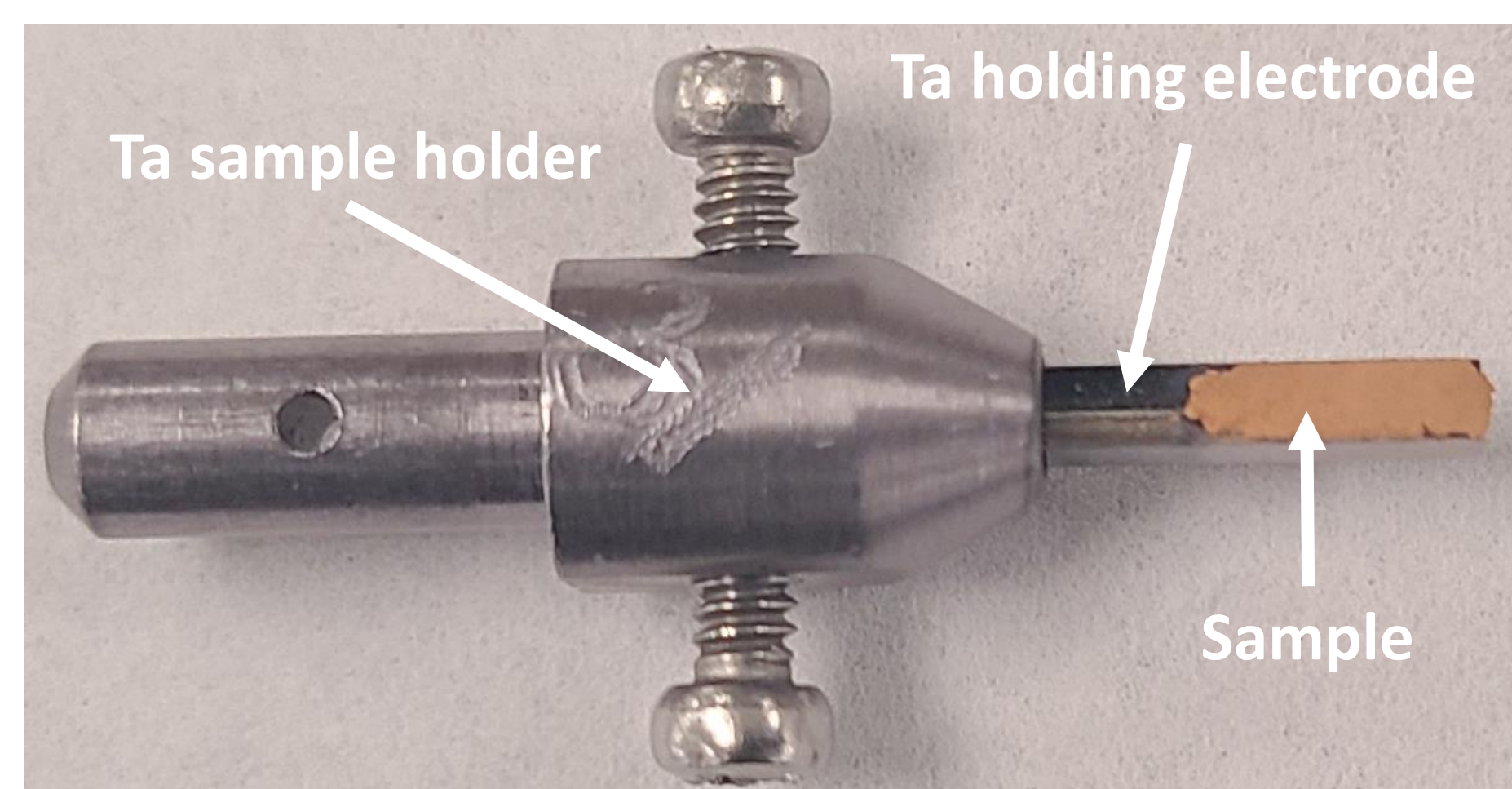


Figure 3. NIST SRM 679 on a Ta holding electrode

Results & Discussion

In Table 1, mean % recovery is reported for all elements with certified values in each reference material. The inter-sample variance in percent recovery (RSD%) is also calculated for each element across reference materials to assess the consistency of measurement accuracy. Out of 49 analyzed elements, 16 were within 10%, 33 were within 25%, and 48 were within a factor of two of the reference values – the expected methodological precision range for Astrum GDMS. More importantly, the inter-sample variances of the measured elements across all five standards were moderately low, with 47 of the 49 elements exhibiting less than 50% variation between the powders.

References

¹Zipkin, A., et al. Red Earth, Green Glass, and Compositional Data: A New Procedure for Solid-State Elemental Characterization, Source Discrimination, and Provenience Analysis of Ochres. *J Archaeol Method Theory* 27, 930–970 (2020).
²Bartov, G., and Putyera, K. New Oxide-Specific RSFs to Improve Non-Conductive Oxide Materials Analysis by GDMS. *Application Note*. <https://www.eag.com/app-note/rsf-to-improve-analysis-by-gdms/>

Table 1. Percent recovery and inter-sample variance in recovery by element.

Element	Inter-sample variance (RSD of % recovery)	Mean % recovery of certified value (n=3 for each standard)				
		IOC-1: Iron Ore	NIST 692: Iron Ore	USGS BCR-2: Basalt	NIST 679: Brick Clay	OREAS 25b: Soil formed over basalt
Li	36%	-	-	128%	59%	115%
Be	52%	-	-	81%	-	175%
Na	34%	-	62%	120%*	62%	102%
Mg	10%	117%	100%	106%*	90%	111%
Al	17%	-	112%	128%*	84%*	118%*
Si	35%	149%*	133%*	63%*	-	99%*
P	21%	250%	230%	-	-	164%
S	50%	-	-	93%	-	194%
K	41%	-	35%	114%*	105%*	87%
Ca	10%	110%	97%	106%*	88%	112%
Sc	9%	-	-	100%	-	114%
Ti	32%	163%	110%	74%*	87%	98%*
V	3%	-	-	100%	-	104%
Cr	30%	115%	-	-	84%	153%
Mn	8%	98%	100%	116%	-	109%
Fe	9%	102%*	107%*	89%*	87%*	98%*
Co	3%	-	-	99%	-	95%
Ni	2%	-	-	99%	-	97%
Cu	4%	-	-	90%	-	84%
Zn	6%	-	-	98%	-	107%
Ga	16%	-	-	112%	-	90%
Ge	3%	-	-	73%	-	76%
As	37%	-	-	138%	-	81%
Rb	2%	-	-	134%	-	138%
Sr	17%	-	-	122%	145%	104%
Y	36%	-	-	113%	-	188%
Zr	18%	-	-	92%	-	119%
Sn	27%	-	-	97%	-	66%
Sb	51%	-	-	88%	-	41%
Ba	24%	-	-	92%	107%	145%
La	49%	-	-	95%	-	194%
Ce	45%	-	-	91%	-	177%
Pr	44%	-	-	94%	-	180%
Nd	42%	-	-	99%	-	181%
Sm	36%	-	-	99%	-	168%
Eu	34%	-	-	96%	-	157%
Gd	14%	-	-	98%	-	119%
Tb	14%	-	-	107%	-	130%
Dy	33%	-	-	96%	-	155%
Ho	24%	-	-	99%	-	140%
Er	26%	-	-	94%	-	135%
Tm	10%	-	-	111%	-	128%
Yb	18%	-	-	98%	-	127%
Lu	33%	-	-	101%	-	162%
Hf	21%	-	-	104%	-	142%
Pb	1%	-	-	109%	-	110%
Bi	7%	-	-	68%	-	76%
Th	39%	-	-	90%	-	158%
U	36%	-	-	93%	-	157%

*Elements ≥1 wt% normally reported as “matrix”; % recovery shown for information only.

Conclusion

Astrum GDMS as used here represents a fast and consistent analytical solution for elemental composition-based provenience studies of natural, complex matrices like ochre. Combined with Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry, also available from EAG Laboratories, we can provide a full scan of elements in solid samples without the need for digestion or fusion. A full scan quantifies weight % elements using LA-ICP-MS and minor and trace elements down to sub-ppm levels using Astrum GDMS, providing the maximum number of variables for multivariate statistical discrimination of sources and assignment of ochre samples of unknown origin.