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RESEARCH ARTICLE | JULY 03 2024

ToF-SIMS spectra of historical inorganic pigments: Copper-, zinc-, arsenic-, and phosphorus-containing pigments in positive polarity

Special Collection: [ToF-SIMS Spectra of Historical Inorganic Pigments](#)

Caroline Bouvier ; Sebastiaan Van Nuffel ; Alain Brunelle  



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ToF-SIMS spectra of historical inorganic pigments: Copper-, zinc-, arsenic-, and phosphorus-containing pigments in positive polarity

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Caroline Bouvier,^{1,2}  Sebastiaan Van Nuffel,^{2,3}  and Alain Brunelle^{1,a)} 

AFFILIATIONS

¹Sorbonne Université, CNRS, Laboratoire d'Archéologie Moléculaire et Structurale (LAMS), Paris 75005, France

²Maastricht MultiModal Molecular Imaging Institute (M4i), Maastricht University, Maastricht 6229ER, The Netherlands

³Faculty of Science and Engineering, Maastricht University, Maastricht 6229EN, The Netherlands

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^{a)}Author to whom correspondence should be addressed: alain.brunelle@cnrs.fr

ABSTRACT

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is increasingly used to analyze cultural heritage materials because it can simultaneously detect organic and inorganic materials while mapping them on a surface. The precise identification of a pigment in a specific layer of a painting or of remaining color on a statue can inform about the technique used or the time of manufacture as well as expose possible forgeries when anachronistic ingredients are identified. Reference spectra are required to confidently identify a given pigment using ToF-SIMS. This paper focuses on eight pigments containing copper, zinc, arsenic, or phosphate, all manufactured following historical recipes. The positive polarity ToF-SIMS reference spectra using a Bi_3^+ primary ion species are presented here. Presented together, these spectra and corresponding tables of secondary ions provide a valuable help in differentiating these pigments, because copper, zinc, arsenic, or phosphate, combined with oxygen, share many mass interferences.

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Accession#: 01939, 01940, 01941, 01942, 01943, 01944, 01945, 01946

Technique: SIMS

Specimen: Peach black, Bone black, Realgar, Bristol yellow medium, Azurite, Malachite, Verdigris, Zinc white

Instrument: IONTOF, TOF SIMS IV

Major Species in Spectra: O, H, C, Cu, Zn, P, Ca, As, S, V, Bi, Cl

Minor Species in Spectra: Hydrocarbon contamination

Published Spectra: 8

Spectral Category: Reference

INTRODUCTION

ToF-SIMS imaging can detect a wide range of elements, so colored minerals can be identified and mapped, given that reference spectra are available for reliable assignment. This paper provides a comparative ToF-SIMS spectral database for eight historical inorganic pigments, containing copper carbonate, zinc oxide or phosphates, vanadium oxide, calcium phosphates, or arsenic sulfide. Numerous possibilities for mass interferences exist between combinations of these elements. Without being able to refer to comparative datasets that provide an overview of the fragment ions for each pigment, it would be difficult to accurately identify one of them as an unknown pigment.

The reference materials were supplied by specialized manufacturers selling pigments reproducing historical recipes as closely as possible, such as Kremer Pigmente GmbH. Pigments were available as finely ground powder of variable particle size (between one and a few tens of μm) conditioned in glass sealed vials. In paintings, pigment particles are dispersed in the binder and not dissolved, so all references were analyzed without any preparation treatment. Natural and synthetic pigments may contain impurities, and specimen compositions described below are the major components as found on the material data sheets provided by the suppliers.

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A stainless-steel spatula was cleaned with propan-2-ol and the powder was directly deposited on a $1 \times 1 \text{ mm}^2$ piece of conductive double-sided tape (3M Electrically Conductive Adhesive Transfer Tape 9703) already fixed to a $1 \text{ cm} \times 1 \text{ cm} \times 0.125 \text{ mm}$ stainless steel plate (17-7PH, Goodfellow Cambridge Limited, UK) fitting the dimensions of the sample holder. A hand press covered with clean aluminum foil was applied onto the powder to fix it to the tape. This allowed to operate in the analysis chamber under ultra-high vacuum (10^{-8} – 10^{-9} hPa) while ensuring a flat surface. For highly toxic pigments, such as the arsenic sulfide Realgar (#01941), a pellet with a flat surface was prepared using a press (Mini-Pellet Press P/N GS03940, Specac Ltd, UK) to limit dust formation.

All spectra were obtained on an IONTOF TOF SIMS IV equipped with a 25 keV bismuth liquid metal ion gun and an Argon gas cluster ion beam (GCIB). Before all analyses, a $500 \times 500 \mu\text{m}^2$ surface was cleaned using 1500–2000 Ar clusters with a kinetic energy of 20 keV (sputter ion dose 2×10^{15} ions/cm²). Analyses were then performed on a $250 \times 250 \mu\text{m}^2$ area centered in this larger cleaned area, rastered over 128×128 pixels using the high current bunched mode. The primary ion dose (25 keV Bi₃⁺) was 4.35×10^{11} ions/cm². Surface potential was compensated and charging of the sample was compensated with the low-energetic 20 eV electrons of the flood gun.

Data were calibrated using sets of peaks as similar as possible for all spectra, using peaks that could be confidently identified. Potassium, copper, zinc, and calcium have distinctive isotopic patterns ensuring confident attribution of the peaks, so #01939 data were calibrated using lists including potassium-containing ions K⁺, K₂⁺, K₂OH⁺, and K₂Cl⁺; #01943, #01944, and #01945 data were calibrated using lists including Na⁺, Cu⁺, Cu₂OH⁺, and Cu₃O⁺ ions; and #01946 data were calibrated using Na⁺, Zn⁺, Zn₂O₂⁺, Zn₃O₃⁺, ⁶⁶Zn⁶⁸ZnZn₂O₄⁺, and ⁶⁶Zn⁶⁸ZnZn₃O₅⁺. Both #01940 and #01942 were calibrated using calcium-containing ions including Ca⁺ and Ca₂O⁺. No bismuth and vanadium-containing ions were used to calibrate #01942 data, since bismuth has no isotope and is close in mass to VP₂O₆. Arsenic sulfide #01941 data were calibrated using ions having high intensity, namely, As⁺, AsS⁺, As₂S₂⁺, AsPbS⁺, and As₃S₃⁺ ions. These calibration lists allowed for a good coverage of the mass range of interest for each specimen, and they are fully detailed in the corresponding tables below.

Pigments contain diverse metallic oxides, hydroxides, carbonates, and even hydrocarbons. They are found inside painting layers that are mostly organic materials. All these compounds do not follow the same ionization processes and have different ionization kinetics.¹ In this context, the choice for the calibration ions is a crucial step to ensure proper peak attribution. If the analytical question aims at identifying the nature of a pigment particle, then the calibration must include inorganic ions, such as the list above, spanning all the mass range of interest, and if possible of the same ion family as those of interest. However, if the analytical question focuses mainly on the identification of organic materials, the calibration must include known low-mass hydrocarbon ions (such as C₂H₃⁺, C₃H₅⁺, C₄H₇⁺, and C₇H₇⁺). The safest strategy when interpreting data from a painting cross-section would be to rely on several calibration sets adapted to the ions of interest and that can be confidently defined independently of the sample's unknowns.

Figures and tables presented below contain the major peaks for positive polarity. Each pigment is uniquely identified thanks to an accession number and they are grouped according to their composition and described in the following section. Their historical relevance is briefly described based on the current literature.^{2–6} Spectrum ID# refers to that number.

SPECIMEN DESCRIPTION (ACCESSION # 01939)

Specimen: Peach black (Kremer Pigmente Ref. 12010)

CAS Registry #: Unknown

Specimen Characteristics: Unknown homogeneity; solid; amorphous; dielectric; inorganic compound; powder;

Chemical Name: Amorphous carbon

Source: Kremer Pigmente GmbH

Specimen Composition: Amorphous carbon (charred peach kernel)

Form: Ground pigment powder

History and Significance: Black pigments derived from charcoals are rarely detectable by the analytical techniques used to investigate pigments such as XRF, while carbon-based black pigments have been used in every society since the domestication of fire. Peach black, for instance, only requires the calcination of kernels. Identifying this pigment is of interest, as they are omnipresent in historical artistic practice. ToF-SIMS is able to map and identify micrometric particles of carbon-based pigments.

As Received Condition: Ground pigment powders were stored in a sealed glass vial in a wooden box, protected from daylight. Stored at room temperature.

Analyzed Region: Areas of $250 \times 250 \mu\text{m}^2$

Ex Situ Preparation/Mounting: Powder was deposited and pressed onto conductive double-sided tape attached to stainless steel $1 \times 1 \text{ cm}^2$ plates. The resulting deposit of powder had a flat surface and was fixed in a suitable way for the vacuum chamber. The plate was directly mounted on a “backmount” sample holder (IONTOF).

In Situ Preparation: None

Charge Control Conditions and Procedures: A low energy electron flood gun was used. Bias voltage between 20 and -30 V . Flood gun filament current 2.35 A. Surface potential was corrected (sample dependent).

Temp. During Analysis: 300 K

Pressure During Analysis: Between 1×10^{-5} and $1 \times 10^{-6} \text{ Pa}$

Pre-analysis Beam Exposure: Ar_{1500–2000}, 20 keV, 2×10^{15} ions/cm²

SPECIMEN DESCRIPTION (ACCESSION # 01940)

Specimen: Bone black (Kremer Pigmente Ref. 47100)

CAS Registry #: 8021-99-6

Specimen Characteristics: Unknown homogeneity; solid; amorphous; dielectric; inorganic compound; powder;

Chemical Name: Bone charcoal

Source: Kremer Pigmente GmbH

Specimen Composition: Amorphous carbon, calcium phosphates

Form: Ground pigment powder

History and Significance: Bone black is made by carbonization of animal bones at temperatures over $400 \text{ }^\circ\text{C}$ but not above $800 \text{ }^\circ\text{C}$. It mainly consists of calcium phosphate and carbonized

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organics. It is very frequently used in paintings, especially in preparation layers.

As Received Condition: Ground pigment powders were stored in a sealed glass vial in a wooden box, protected from daylight. Stored at room temperature.

Analyzed Region: Areas of $250 \times 250 \mu\text{m}^2$

Ex Situ Preparation/Mounting: Powder was deposited and pressed onto conductive double-sided tape attached to stainless steel $1 \times 1 \text{ cm}^2$ plates. The resulting deposit of powder had a flat surface and was fixed in a suitable way for the vacuum chamber. The plate was directly mounted on a “backmount” sample holder (IONTOF).

In Situ Preparation: None

Charge Control Conditions and Procedures: A low energy electron flood gun was used. Bias voltage between 20 and -30 V . Flood gun filament current 2.35 A. Surface potential was corrected (sample dependent).

Temp. During Analysis: 300 K

Pressure During Analysis: Between 1×10^{-5} and $1 \times 10^{-6} \text{ Pa}$

Pre-analysis Beam Exposure: $\text{Ar}_{1500-2000}$, 20 keV, $2 \times 10^{15} \text{ ions/cm}^2$

SPECIMEN DESCRIPTION (ACCESSION # 01941)

Specimen: Realgar/red orpiment (Kremer Pigmente Ref. 10800)

CAS Registry #: 1303-33-9

Specimen Characteristics: Unknown homogeneity; solid; unknown crystallinity; dielectric; inorganic compound; powder;

Chemical Name: Arsenic (III) sulfide (natural mineral)

Source: Kremer Pigmente GmbH

Specimen Composition: Natural arsenic sulfide $\alpha\text{-As}_4\text{S}_4$

Form: Ground pigment powder

History and Significance: A mineral prized for its bright red color that was used until the beginning of the 19th century. Found in volcanic and geothermal regions, and its geographic origin varies. It was found in luxurious articles in antiquity to show opulence and was used as ritual offerings and in cosmetics, despite its high toxicity. It exists in rare natural and synthetic forms. Its occurrence is difficult to investigate due to light instability, converting it to yellow pararealgar (As_4S_4), thereby often mistaken for other yellow As pigments unless crystalline phases can be differentiated by the analytical techniques used. Red realgar can be found in environments where the absence of light preserves it.

As Received Condition: Ground pigment powders were stored in a sealed glass vial in a wooden box, protected from daylight. Stored at room temperature.

Analyzed Region: Areas of $250 \times 250 \mu\text{m}^2$

Ex Situ Preparation/Mounting: Because of the toxicity of arsenic sulfide, a pellet was prepared using a Specac Mini Pellet Press. A flat surface was obtained, and dust formation was limited when handling the sample. The pellet was directly mounted on a “backmount” sample holder (IONTOF).

In Situ Preparation: None

Charge Control Conditions and Procedures: A low energy electron flood gun was used. Bias voltage between 20 and -30 V . Flood gun filament current 2.35 A. Surface potential was corrected (sample dependent).

Temp. During Analysis: 300 K

Pressure During Analysis: Between 1×10^{-5} and $1 \times 10^{-6} \text{ Pa}$

Pre-analysis Beam Exposure: $\text{Ar}_{1500-2000}$, 20 keV, $2 \times 10^{15} \text{ ions/cm}^2$

SPECIMEN DESCRIPTION (ACCESSION # 01942)

Specimen: Bristol yellow medium (Kremer Pigmente Ref. 43111)

CAS Registry #: 7779-90-0, 14059-33-7

Specimen Characteristics: Inhomogeneous; solid; unknown crystallinity; dielectric; inorganic compound; powder;

Chemical Name: Trizinc bis(ortho)phosphate + Bismuth vanadium tetraoxide

Source: Kremer Pigmente GmbH

Specimen Composition: $\text{Zn}_3(\text{PO}_4)_2 + \text{BiVO}_4$

Form: Ground pigment powder

History and Significance: Due to their toxicity, lead pigments have been gradually prohibited over the past two centuries. Alternative yellow pigments such as modified bismuth yellows (Bristol yellows) were produced to replace them. Bristol yellows have been used since the 20th century to imitate Naples yellow as they have similar optical properties. Copper and zinc compounds can have mass interference with Bristol Yellow ions, so their distinction is of interest.

As Received Condition: Ground pigment powders were stored in a sealed glass vial in a wooden box, protected from daylight. Stored at room temperature.

Analyzed Region: Areas of $250 \times 250 \mu\text{m}^2$

Ex Situ Preparation/Mounting: Powder was deposited and pressed onto conductive double-sided tape attached to stainless steel $1 \times 1 \text{ cm}^2$ plates. The resulting deposit of powder had a flat surface and was fixed in a suitable way for the vacuum chamber. The plate was directly mounted on a “backmount” sample holder (IONTOF).

In Situ Preparation: None

Charge Control Conditions and Procedures: A low energy electron flood gun was used. Bias voltage between 20 and -30 V . Flood gun filament current 2.35 A. Surface potential was corrected (sample dependent).

Temp. During Analysis: 300 K

Pressure During Analysis: Between 1×10^{-5} and $1 \times 10^{-6} \text{ Pa}$

Pre-analysis Beam Exposure: $\text{Ar}_{1500-2000}$, 20 keV, $2 \times 10^{15} \text{ ions/cm}^2$

SPECIMEN DESCRIPTION (ACCESSION # 01943)

Specimen: Azurite (Kremer Pigmente Ref. 10207)

CAS Registry #: 12069-69-1

Specimen Characteristics: Inhomogeneous; solid; unknown crystallinity; dielectric; inorganic compound; powder;

Chemical Name: Basic copper (II) carbonate

Source: Kremer Pigmente GmbH

Specimen Composition: $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$

Form: Ground pigment powder

History and Significance: A natural blue to turquoise-blue-green copper carbonate that results from the erosion of copper deposits. It was used in many contexts over the centuries and was considered a fairly precious material.

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As Received Condition: Ground pigment powders were stored in a sealed glass vial in a wooden box, protected from daylight. Stored at room temperature.

Analyzed Region: Areas of $250 \times 250 \mu\text{m}^2$

Ex Situ Preparation/Mounting: Powder was deposited and pressed onto conductive double-sided tape attached to stainless steel $1 \times 1 \text{ cm}^2$ plates. The resulting deposit of powder had a flat surface and was fixed in a suitable way for the vacuum chamber. The plate was directly mounted on a “backmount” sample holder (IONTOF).

In Situ Preparation: None

Charge Control Conditions and Procedures: A low energy electron flood gun was used. Bias voltage between 20 and -30 V . Flood gun filament current 2.35 A. Surface potential was corrected (sample dependent).

Temp. During Analysis: 300 K

Pressure During Analysis: Between 1×10^{-5} and $1 \times 10^{-6} \text{ Pa}$

Pre-analysis Beam Exposure: $\text{Ar}_{1500-2000}$, 20 keV, $2 \times 10^{15} \text{ ions/cm}^2$

SPECIMEN DESCRIPTION (ACCESSION # 01944)

Specimen: Malachite, natural (Kremer Pigmente Ref. 10300)

CAS Registry #: 1319-53-5

Specimen Characteristics: Inhomogeneous; solid; unknown crystallinity; dielectric; inorganic compound; powder;

Chemical Name: Basic cupric carbonate

Source: Kremer Pigmente GmbH

Specimen Composition: $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$

Form: Ground pigment powder

History and Significance: A natural green to turquoise-green copper carbonate, which results from the erosion of copper deposits. It is one of the earliest known bright green pigments, and a dominant one until the mid-18th century. It was considered a fairly precious material. It consists of rather large spherical particles.

As Received Condition: Ground pigment powders were stored in a sealed glass vial in a wooden box, protected from daylight. Stored at room temperature.

Analyzed Region: Areas of $250 \times 250 \mu\text{m}^2$

Ex Situ Preparation/Mounting: Powder was deposited and pressed onto conductive double-sided tape attached to stainless steel $1 \times 1 \text{ cm}^2$ plates. The resulting deposit of powder had a flat surface and was fixed in a suitable way for the vacuum chamber. The plate was directly mounted on a “backmount” sample holder (IONTOF).

In Situ Preparation: None

Charge Control Conditions and Procedures: A low energy electron flood gun was used. Bias voltage between 20 and -30 V . Flood gun filament current 2.35 A. Surface potential was corrected (sample dependent).

Temp. During Analysis: 300 K

Pressure During Analysis: Between 1×10^{-5} and $1 \times 10^{-6} \text{ Pa}$

Pre-analysis Beam Exposure: $\text{Ar}_{1500-2000}$, 20 keV, $2 \times 10^{15} \text{ ions/cm}^2$

SPECIMEN DESCRIPTION (ACCESSION # 01945)

Specimen: Verdigris, synthetic (Kremer Pigmente Ref. 44450)

CAS Registry #: 6046-93-1

Specimen Characteristics: Inhomogeneous; solid; unknown crystallinity; dielectric; inorganic compound; powder;

Chemical Name: Copper-(II)-acetate-1-hydrate

Source: Kremer Pigmente GmbH

Specimen Composition: $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot [\text{Cu}(\text{OH})_2]_3 \cdot 2\text{H}_2\text{O}$

Form: Ground pigment powder

History and Significance: A family of synthetic pigments, containing variations of copper acetate, with green to blue-green hues. Synthesized since Antiquity, it is an acetate copper salt produced by the reaction of acetic acid with copper and has been particularly common in wine-growing regions. It has a characteristic vinegar odor. A better knowledge of the ion signal of Verdigris pigments is of interest. Indeed, considered unstable, it reacts with binders and other pigments forming soaps and other copper salts, respectively, making its identification in a painting often ambiguous. Degradation products result in a brown tint.

As Received Condition: Ground pigment powders were stored in a sealed glass vial in a wooden box, protected from daylight. Stored at room temperature.

Analyzed Region: Areas of $250 \times 250 \mu\text{m}^2$

Ex Situ Preparation/Mounting: Powder was deposited and pressed onto conductive double-sided tape attached to stainless steel $1 \times 1 \text{ cm}^2$ plates. The resulting deposit of powder had a flat surface and was fixed in a suitable way for the vacuum chamber. The plate was directly mounted on a “backmount” sample holder (IONTOF).

In Situ Preparation: None

Charge Control Conditions and Procedures: A low energy electron flood gun was used. Bias voltage between 20 and -30 V . Flood gun filament current 2.35 A. Surface potential was corrected (sample dependent).

Temp. During Analysis: 300 K

Pressure During Analysis: Between 1×10^{-5} and $1 \times 10^{-6} \text{ Pa}$

Pre-analysis Beam Exposure: $\text{Ar}_{1500-2000}$, 20 keV, $2 \times 10^{15} \text{ ions/cm}^2$

SPECIMEN DESCRIPTION (ACCESSION # 01946)

Specimen: Zinc white (Kremer Pigmente Ref. 46300)

CAS Registry #: 1314-13-2

Specimen Characteristics: Inhomogeneous; solid; unknown crystallinity; dielectric; inorganic compound; powder;

Chemical Name: Zinc oxide

Source: Kremer Pigmente GmbH

Specimen Composition: ZnO

Form: Ground pigment powder

History and Significance: A widely used substitute for lead-containing whites that was first produced in the 19th century by Winsor & Newton (1834) with Michael Faraday.

As Received Condition: Ground pigment powders were stored in a sealed glass vial in a wooden box, protected from daylight. Stored at room temperature.

Analyzed Region: Areas of $250 \times 250 \mu\text{m}^2$

Ex Situ Preparation/Mounting: Powder was deposited and pressed onto conductive double-sided tape attached to stainless steel $1 \text{ cm} \times 1 \text{ cm}$ plates. The resulting deposit of powder had a flat surface and was fixed in a suitable way for the vacuum

chamber. The plate was directly mounted on a “backmount” sample holder (IONTOF).

In Situ Preparation: None

Charge Control Conditions and Procedures: A low energy electron flood gun was used. Bias voltage between 20 and -30 V. Flood gun filament current 2.35 A. Surface potential was corrected (sample dependent).

Temp. During Analysis: 300 K

Pressure During Analysis: Between 1×10^{-5} and 1×10^{-6} Pa

Pre-analysis Beam Exposure: $\text{Ar}_{1500-2000}$, 20 keV, 2×10^{15} ions/cm²

INSTRUMENT CONFIGURATION

Manufacturer and Model: IONTOF, TOF SIMS IV

Analyzer Type: Time-of-flight

Sample Rotation: No

Rotation Rate: 0 rpm

Oxygen Flood Source: None

Oxygen Flood Pressure: N/A

Other Flood Source: None

Other Flood Pressure: N/A

Unique Instrument Features Used: None

Energy Acceptance Window: 20 eV

Post-acceleration Voltage: 10 000 eV

Sample Bias: 10–20 eV

Specimen Normal-to-analyzer (Θ_e): 0°

Ion sources

Ion source 1 of 2

Purpose of this Ion Source: Analysis beam

Ion Source Manufacturer: IONTOF GmbH

Ion Source Model: Liquid metal ion gun (LMIG) with bismuth cluster (25 keV)

Beam Mass Filter: Yes

Beam Species and Charge State: Bi_3^+

Beam Gating Used: Double pulsed + Bunched

Additional Beam Comments: None

Beam Voltage: 25 000 eV

Net Beam Voltage (impact voltage): 25 000 eV

Ion Pulse Width: 0.8–1.2 ns

Ion Pulse Rate: 5–10 kHz

DC Beam Current: ~ 10 nA

Pulsed Beam Current: ~ 0.0004 nA

Current Measurement Method: Faraday cup

Beam Diameter: ~ 2 μm

Beam Raster Size: 250×250 μm^2

Raster Pixel Dimensions: 128×128

Beam Incident Angle: 45°

Source-to-Analyzer Angle: 45°

Ion source 2 of 2

Purpose of this Ion Source: Sputtering beam

Ion Source Manufacturer: IONTOF GmbH

Ion Source Model: Argon GCIB

Beam Mass Filter: Yes

Beam Species and Charge State: Ar_n^+ with $n = 1500-2000$

Beam Gating Used: Wien filter

Additional Beam Comments: Used as sputter gun, not analysis mode.

Beam Voltage: 20 000 eV

Net Beam Voltage (impact voltage): 20 000 eV

Ion Pulse Width: N/A

Ion Pulse Rate: N/A

DC Beam Current: ~ 10 nA

Pulsed Beam Current: N/A

Current Measurement Method: Faraday cup

Beam Diameter: ~ 50 μm

Beam Raster Size: 500×500 μm^2

Raster Pixel Dimensions: N/A

Beam Incident Angle: 45°

Source-to-Analyzer Angle: 45°

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Caroline Bouvier: Investigation (lead); Writing – original draft (lead). **Sebastiaan Van Nuffel:** Investigation (equal); Writing – review & editing (lead). **Alain Brunelle:** Conceptualization (lead); Supervision (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

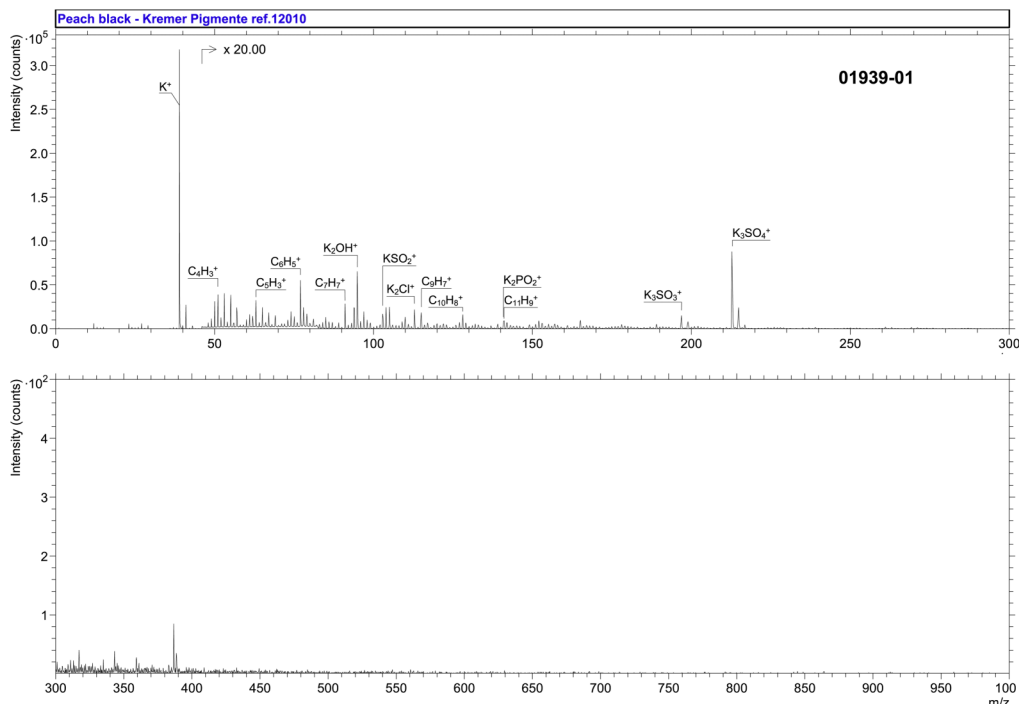
REFERENCES

- 1 R. G. Cooks and K. L. Bush, *Int. J. Mass Spectrom. Ion Phys.* **53**, 111 (1983).
- 2 N. Eastaugh, V. Walsh, T. Chaplin, and R. Siddall, *Pigment Compendium: A Dictionary and Optical Microscopy of Historical Pigments*, 1st ed. (Routledge, London, 2008).
- 3 E. Robert and L. Feller, *Artists' Pigments: A Handbook of Their History and Characteristics, Vol. 1* (Archetype Publications, London, 1986).
- 4 A. Roy, *Artists' Pigments: A Handbook of Their History and Characteristics, Vol. 2* (Archetype Publications, London, 1993).
- 5 E. W. FitzHugh, *Artists' Pigments: A Handbook of Their History and Characteristics, Vol. 3* (Archetype Publications, London, 1997).
- 6 J. R. Barnett, S. Miller, and E. Pearce, *Opt. Laser Technol.* **38**, 445 (2006).
- 7 L. M. Smieska, R. Mullett, L. Ferri, and A. R. Woll, *Appl. Phys. A* **123**, 1 (2017).
- 8 M. Price, *Leonardo* **33**, 281 (2000).

SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01939-01	38.963 (4.42)	K^+	–
	51.022 (–12.4)	$C_4H_3^+$	Charcoal
	63.022 (–13.6)	$C_5H_3^+$	Charcoal
	77.042 (37.9)	$C_6H_5^+$	Charcoal
	91.053 (–14.9)	$C_7H_7^+$	Charcoal
	94.927 (–31.1)	K_2OH^+	–
	102.925 (–4.01)	KSO_2^+	–
	112.896 (1.74)	K_2Cl^+	–
	115.052 (–15.7)	$C_9H_7^+$	Charcoal
	128.062 (2.43)	$C_{10}H_8^+$	Charcoal
	140.886 (–29.7)	$K_2PO_2^+$	–
	141.067 (–21.4)	$C_{11}H_9^+$	Charcoal
	196.840 (–35.0)	$K_3SO_3^+$	–
	212.834 (–40.0)	$K_3SO_4^+$	–

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Accession #:

01939-01

<p>■ Specimen: ■ Technique: Instrument: Analyzer Type: Analyzer Mass Resolving Power: Mass Resolving Power Determined at: Species Used for Mass Calibration: Specimen Normal-to-Analyzer: Source-to-Analyzer Angle: Primary Beam Ion Gun: Primary Ion Species: Primary Ion Dose: Primary Ion Pulse Width: Primary Ion Pulse Rate: Net Beam Voltage: Pulsed Beam Current: DC Beam Current: Beam Diameter: Beam Raster Size: Beam Incident Angle: Secondary Source Polarity: Mass Range Minimum: Mass Range Maximum: Spectrum Dead Time Corrected: Total Spectral Acquisition Time: Comment:</p>	<p>Peach Black—Kremer Pigmente Ref. 12010 SIMS IONTOF, TOF SIMS IV Time-of-flight 1200 m/Δm 27 Da $C^+, K^+, K_2^+, K_2OH^+, K_2Cl^+$ 0° 45° LMIG Bi_3^+ 4.35×10^{11} ion/cm² 0.8–1.2 ns 5 kHz 25 000 eV 0.000 13 nA 10.4 nA $\sim 2 \mu m$ $250 \times 250 \mu m^2$ 45° Positive 0 Da 3545 Da Yes 335 s</p>
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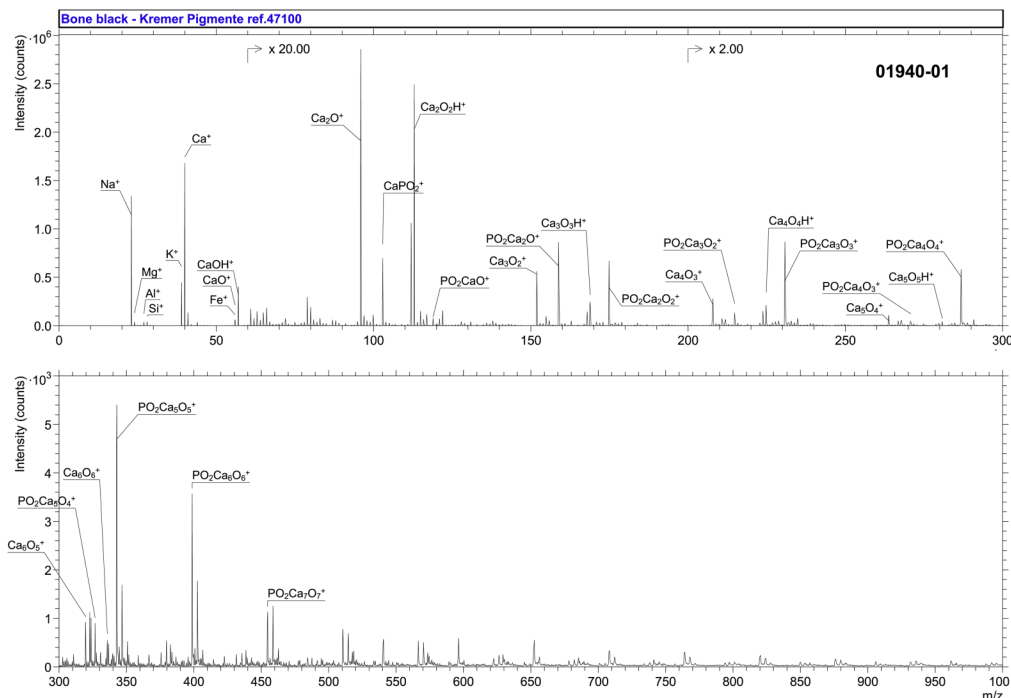
The peak at m/z 102.925 attributed to KSO_2^+ can be distinguished from the peak at m/z 102.925 attributed to $CaPO_2^+$ found in Bone Black (#01940) using isotopic pattern matching.

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SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01940-01	22.990 (23.4)	Na ⁺	–
	23.984 (–20.6)	Mg ⁺	–
	26.981 (–12.7)	Al ⁺	–
	27.977 (7.35)	Si ⁺	–
	38.963 (3.53)	K ⁺	–
	39.962 (7.67)	Ca ⁺	Calcium phosphate
	55.934 (–6.43)	Fe ⁺	–
	55.956 (–14.7)	CaO ⁺	–
	56.964 (–12.6)	CaOH ⁺	Calcium phosphate
	95.919 (–8.30)	Ca(CaO) ⁺	Calcium phosphate
	102.925 (–7.34)	CaPO ₂ ⁺	Calcium phosphate
	112.921 (–8.34)	(CaO) ₂ H ⁺	Calcium phosphate
	118.922 (9.49)	PO ₂ CaO ⁺	Calcium phosphate
	151.877 (–1.23)	Ca(CaO) ₂ ⁺	Calcium phosphate
	158.884 (5.26)	PO ₂ Ca ₂ O ⁺	Calcium phosphate
	168.880 (–3.83)	(CaO) ₃ H ⁺	Calcium phosphate
	174.880 (8.25)	PO ₂ Ca ₂ O ₂ ⁺	Calcium phosphate
	207.836 (5.63)	Ca(CaO) ₃ ⁺	Calcium phosphate
	214.843 (11.0)	PO ₂ Ca ₃ O ₂ ⁺	Calcium phosphate
	224.837 (0.48)	(CaO) ₄ H ⁺	Calcium phosphate
	230.838 (8.71)	PO ₂ Ca ₃ O ₃ ⁺	Calcium phosphate
	263.793 (3.21)	Ca(CaO) ₄ ⁺	Calcium phosphate
	270.802 (15.8)	PO ₂ Ca ₄ O ₃ ⁺	Calcium phosphate
	280.796 (3.47)	(CaO) ₅ H ⁺	Calcium phosphate
	286.794 (2.04)	PO ₂ Ca ₄ O ₄ ⁺	Calcium phosphate
	319.751 (5.56)	Ca(CaO) ₅ ⁺	Calcium phosphate
	326.761 (16.6)	PO ₂ Ca ₅ O ₄ ⁺	Calcium phosphate
336.754 (3.66)	(CaO) ₆ H ⁺	Calcium phosphate	
342.753 (6.05)	PO ₂ Ca ₅ O ₅ ⁺	Calcium phosphate	
398.711 (7.16)	PO ₂ Ca ₆ O ₆ ⁺	Calcium phosphate	
454.678 (26.3)	PO ₂ Ca ₇ O ₇ ⁺	Calcium phosphate	

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Accession #:

01940-01

<p>■ Specimen: ■ Technique: Instrument: Analyzer Type: Analyzer Mass Resolving Power: Mass Resolving Power Determined at: Species Used for Mass Calibration: Specimen Normal-to-Analyzer: Source-to-Analyzer Angle: Primary Beam Ion Gun: Primary Ion Species: Primary Ion Dose: Primary Ion Pulse Width: Primary Ion Pulse Rate: Net Beam Voltage: Pulsed Beam Current: DC Beam Current: Beam Diameter: Beam Raster Size: Beam Incident Angle: Secondary Source Polarity: Mass Range Minimum: Mass Range Maximum: Spectrum Dead Time Corrected: Total Spectral Acquisition Time: Comment:</p>	<p>Bone Black—Kremer Pigmente Ref. 47100 SIMS IONTOF, TOF SIMS IV Time-of-flight 3500 m/Δm 27 Da $\text{Na}^+, \text{Ca}^+, \text{Ca}_2\text{O}^+, \text{Ca}_3\text{O}_2^+, \text{Ca}_4\text{O}_3^+, \text{Ca}_5\text{O}_4^+, \text{Ca}_6\text{O}_5^+$ 0° 45° LMIG Bi_3^+ 4.37×10^{11} ion/cm² 0.8–1.2 ns 5 kHz 25 000 eV 0.000 15 nA 14.7 nA $\sim 2 \mu\text{m}$ $250 \times 250 \mu\text{m}^2$ 45° Positive 0 Da 3545 Da Yes 292 s</p>
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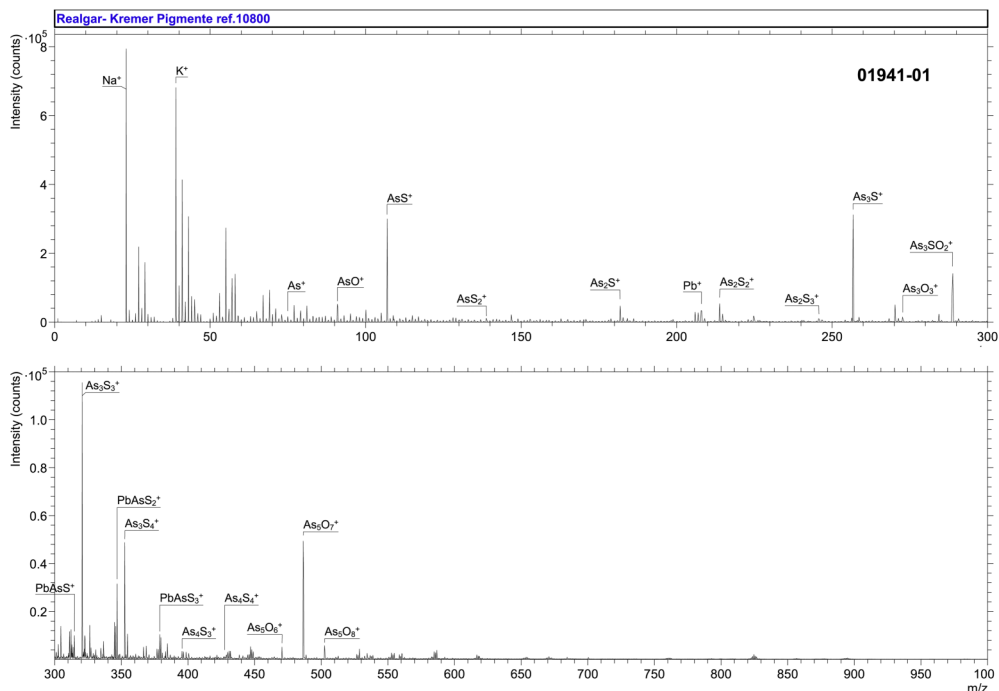
The peak at m/z 102.925 attributed to CaPO_2^+ can be distinguished from the peak at m/z 102.925 attributed to KSO_2^+ found in Peach Black (#01939) using isotopic pattern matching.

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SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01941-01	74.922 (13.4)	As ⁺	α -As ₄ S ₄
	90.914 (-22.6)	AsO ⁺	Arsenic oxide
	106.891 (-27.9)	AsS ⁺	α -As ₄ S ₄
	138.863 (-15.7)	AsS ₂ ⁺	α -As ₄ S ₄
	181.814 (-6.79)	As ₂ S ⁺	α -As ₄ S ₄
	207.972 (-17.8)	Pb ⁺	Natural impurity
	213.783 (-16.5)	As ₂ S ₂ ⁺	α -As ₄ S ₄
	245.756 (-10.3)	As ₂ S ₃ ⁺	α -As ₄ S ₄
	256.734 (-8.30)	As ₃ S ⁺	α -As ₄ S ₄
	272.748 (-3.46)	As ₃ O ₃ ⁺	Arsenic oxide
	288.726 (-0.90)	As ₃ SO ₂ ⁺	α -As ₄ S ₄ /arsenic oxide
	314.871 (4.83)	PbAsS ⁺	Natural impurity
	320.678 (-7.97)	As ₃ S ₃ ⁺	α -As ₄ S ₄
	346.832 (-27.5)	PbAsS ₂ ⁺	Natural impurity
	352.653 (1.19)	As ₃ S ₄ ⁺	α -As ₄ S ₄
	378.807 (-19.5)	PbAsS ₃ ⁺	Natural impurity
	395.601 (-2.70)	As ₄ S ₃ ⁺	α -As ₄ S ₄
	427.583 (19.8)	As ₄ S ₄ ⁺	α -As ₄ S ₄
	470.576 (-1.02)	As ₅ O ₆ ⁺	α -As ₄ S ₄ /arsenic oxide
	486.578 (12.6)	As ₅ O ₇ ⁺	α -As ₄ S ₄ /arsenic oxide
502.575 (15.5)	As ₅ O ₈ ⁺	α -As ₄ S ₄ /arsenic oxide	

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Accession #:

01941-01

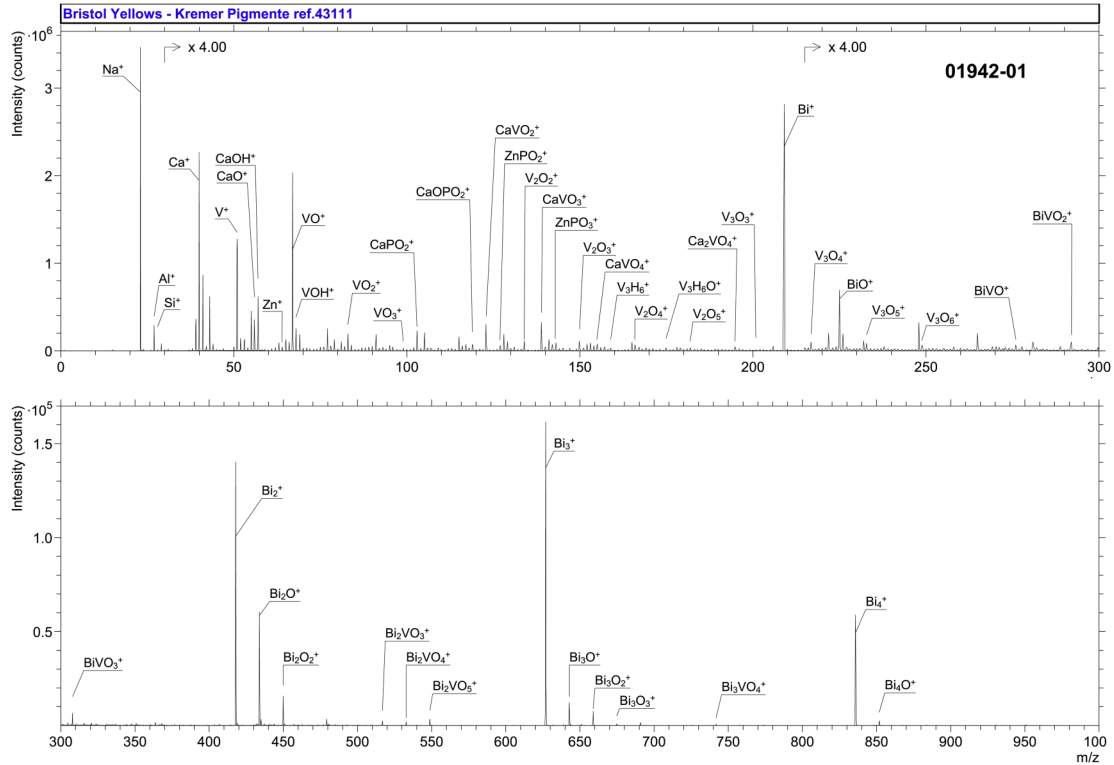
<p>■ Specimen: ■ Technique: Instrument: Analyzer Type: Analyzer Mass Resolving Power: Mass Resolving Power Determined at: Species Used for Mass Calibration: Specimen Normal-to-Analyzer: Source-to-Analyzer Angle: Primary Beam Ion Gun: Primary Ion Species: Primary Ion Dose: Primary Ion Pulse Width: Primary Ion Pulse Rate: Net Beam Voltage: Pulsed Beam Current: DC Beam Current: Beam Diameter: Beam Raster Size: Beam Incident Angle: Secondary Source Polarity: Mass Range Minimum: Mass Range Maximum: Spectrum Dead Time Corrected: Total Spectral Acquisition Time: Comment:</p>	<p>Realgar/red orpiment—Kremer Pigmente Ref. 10800 SIMS IONTOF, TOF SIMS IV Time-of-flight 3900 m/Δm 27 Da As⁺, AsS⁺, As₂S₂⁺, AsPbS⁺, As₃S₃⁺ 0° 45° LMIG Bi₃⁺ 4.34 × 10¹¹ ion/cm² 0.8–1.2 ns 5 kHz 25 000 eV 0.000 21 nA 14.4 nA ~2 μm 250 × 250 μm² 45° Positive 0 Da 3545 Da Yes 207 s</p> <p>Unstable, sensitive to light and oxygen. All oxygen-containing ions were localized in the same round-shaped areas of about 10 μm diameter dispersed on the surface, allowing us to confidently determine if a species contained oxygen or only sulfur.</p>
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SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01942-01	22.990 (31.5)	Na ⁺	–
	26.981 (–4.76)	Al ⁺	–
	27.976 (–9.51)	Si ⁺	–
	39.962 (5.09)	Ca ⁺	–
	46.967 (–32.1)	PO ⁺	Zn ₃ (PO ₄) ₂
	50.943 (–10.6)	V ⁺	BiVO ₄
	55.956 (–20.7)	CaO ⁺	–
	56.964 (–9.73)	CaOH ⁺	–
	63.928 (–8.30)	Zn ⁺	–
	66.939 (5.90)	VO ⁺	BiVO ₄
	67.947 (8.58)	VOH ⁺	BiVO ₄
	82.937 (47.8)	VO ₂ ⁺	BiVO ₄
	98.931 (29.6)	VO ₃ ⁺	BiVO ₄
	102.923 (–2.82)	CaPO ₂ ⁺	–
	118.921 (–0.26)	CaOPO ₂ ⁺	–
	122.896 (–2.51)	CaVO ₂ ⁺	–
	126.893 (2.89)	ZnPO ₂ ⁺	Zn ₃ (PO ₄) ₂
	133.876 (–8.97)	V ₂ O ₂ ⁺	BiVO ₄
	138.893 (14.5)	CaVO ₃ ⁺	–
	142.889 (9.85)	ZnPO ₃ ⁺	Zn ₃ (PO ₄) ₂
	149.872 (–0.98)	V ₂ O ₃ ⁺	BiVO ₄
	154.889 (21.3)	CaVO ₄ ⁺	–
	158.881 (18.5)	V ₃ H ₆ ⁺	BiVO ₄
	165.869 (10.5)	V ₂ O ₄ ⁺	BiVO ₄
	174.875 (11.1)	V ₃ H ₆ O ⁺	BiVO ₄
	181.865 (16.2)	V ₂ O ₅ ⁺	BiVO ₄
	194.846 (–9.93)	Ca ₂ VO ₄ ⁺	–
	200.816 (–1.53)	V ₃ O ₃ ⁺	BiVO ₄
	208.984 (18.6)	Bi ⁺	BiVO ₄
	216.814 (13.1)	V ₃ O ₄ ⁺	BiVO ₄
	224.977 (11.4)	BiO ⁺	BiVO ₄
	232.810 (16.5)	V ₃ O ₅ ⁺	BiVO ₄
	248.806 (19.8)	V ₃ O ₆ ⁺	BiVO ₄
	275.913 (–21.0)	BiVO ⁺	BiVO ₄
	291.913 (–2.34)	BiVO ₂ ⁺	BiVO ₄
	307.907 (–3.46)	BiVO ₃ ⁺	BiVO ₄
	417.967 (17.0)	Bi ₂ ⁺	BiVO ₄
	433.961 (14.6)	Bi ₂ O ⁺	BiVO ₄
	449.960 (21.2)	Bi ₂ O ₂ ⁺	BiVO ₄
	516.893 (7.63)	Bi ₂ VO ₃ ⁺	BiVO ₄
	532.895 (21.1)	Bi ₂ VO ₄ ⁺	BiVO ₄
	548.869 (–18.6)	Bi ₂ VO ₅ ⁺	BiVO ₄
626.957 (26.1)	Bi ₃ ⁺	BiVO ₄	
642.941 (8.81)	Bi ₃ O ⁺	BiVO ₄	
658.935 (7.13)	Bi ₃ O ₂ ⁺	BiVO ₄	
674.930 (6.75)	Bi ₃ O ₃ ⁺	BiVO ₄	
741.873 (11.8)	Bi ₃ VO ₄ ⁺	BiVO ₄	
835.936 (18.5)	Bi ₄ ⁺	BiVO ₄	
851.922 (7.25)	Bi ₄ O ⁺	BiVO ₄	

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Accession #:

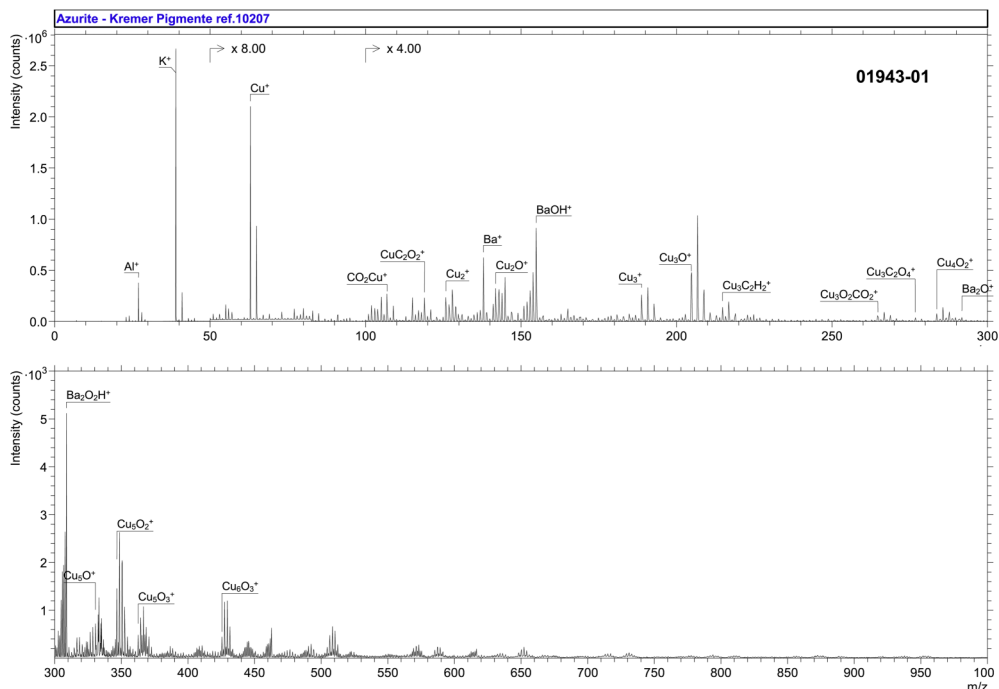
01942-01

■ Specimen:	Bristol Yellow—Kremer Pigmente Ref. 43111
■ Technique:	SIMS
Instrument:	IONTOF, TOF SIMS IV
Analyzer Type:	Time-of-flight
Analyzer Mass Resolving Power:	3500 $m/\Delta m$
Mass Resolving Power Determined at:	25 Da
Species Used for Mass Calibration:	Na^+ , Ca^+ , Ca_2O^+ , $\text{Ca}_5\text{O}_5\text{H}^+$, $\text{Ca}_6\text{O}_6\text{H}^+$
Specimen Normal-to-Analyzer:	0°
Source-to-Analyzer Angle:	45°
Primary Beam Ion Gun:	LMIG
Primary Ion Species:	Bi_3^+
Primary Ion Dose:	4.35×10^{11} ion/cm ²
Primary Ion Pulse Width:	0.8–1.2 ns
Primary Ion Pulse Rate:	5 kHz
Net Beam Voltage:	25 000 eV
Pulsed Beam Current:	0.000 17 nA
DC Beam Current:	15.1 nA
Beam Diameter:	~2 μm
Beam Raster Size:	250 × 250 μm^2
Beam Incident Angle:	45°
Secondary Source Polarity:	Positive
Mass Range Minimum:	0 Da
Mass Range Maximum:	3545 Da
Spectrum Dead Time Corrected:	Yes
Total Spectral Acquisition Time:	256 s

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SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01943-01	26.980 (-31.2)	Al ⁺	-
	38.965 (42.0)	K ⁺	-
	62.928 (-10.3)	Cu ⁺	Cu ₃ (CO ₃) ₂ (OH) ₂
	106.915 (-34.4)	CO ₂ Cu ⁺	Cu ₃ (CO ₃) ₂ (OH) ₂
	118.913 (-49.5)	CuC ₂ O ₂ ⁺	Cu ₃ (CO ₃) ₂ (OH) ₂
	125.857 (-10.8)	Cu ₂ ⁺	Cu ₃ (CO ₃) ₂ (OH) ₂
	137.901 (-23.8)	Ba ⁺	Ba-rich impurity found in natural azurite ⁷
	141.852 (-11.4)	Cu ₂ O ⁺	Cu ₃ (CO ₃) ₂ (OH) ₂
	154.906 (-7.22)	BaOH ⁺	Ba-rich impurity found in natural azurite
	188.790 (6.94)	Cu ₃ ⁺	Cu ₃ (CO ₃) ₂ (OH) ₂
	204.781 (-10.8)	Cu ₃ O ⁺	Cu ₃ (CO ₃) ₂ (OH) ₂
	214.810 (27.4)	Cu ₃ C ₂ H ₂ ⁺	Cu ₃ (CO ₃) ₂ (OH) ₂
	264.762 (-22.7)	Cu ₃ O ₂ CO ₂ ⁺	Cu ₃ (CO ₃) ₂ (OH) ₂
	276.777 (34.4)	Cu ₃ C ₂ O ₄ ⁺	Cu ₃ (CO ₃) ₂ (OH) ₂
	283.701 (-24.9)	Cu ₄ O ₂ ⁺	Cu ₃ (CO ₃) ₂ (OH) ₂
	291.802 (-8.48)	Ba ₂ O ⁺	Ba-rich impurity found in natural azurite
	308.800 (-23.7)	Ba ₂ O ₂ H ⁺	Ba-rich impurity found in natural azurite
	330.648 (15.7)	Cu ₅ O ⁺	Cu ₃ (CO ₃) ₂ (OH) ₂
	346.631 (-18.8)	Cu ₅ O ₂ ⁺	Cu ₃ (CO ₃) ₂ (OH) ₂
	362.625 (-20.1)	Cu ₅ O ₃ ⁺	Cu ₃ (CO ₃) ₂ (OH) ₂
425.551 (-26.1)	Cu ₆ O ₃ ⁺	Cu ₃ (CO ₃) ₂ (OH) ₂	



Accession #:

01943-01

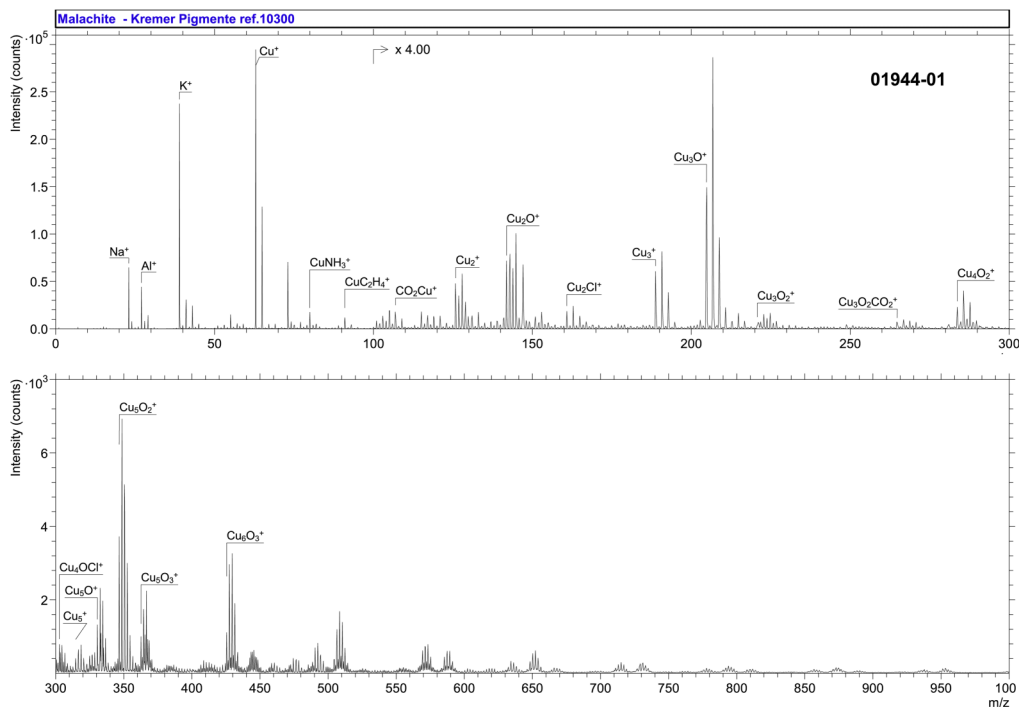
■ Specimen:	Azurite—Kremer Pigmente Ref. 10207
■ Technique:	SIMS
Instrument:	IONTOF, TOF SIMS IV
Analyzer Type:	Time-of-flight
Analyzer Mass Resolving Power:	2000 m/Δm
Mass Resolving Power Determined at:	27 Da
Species Used for Mass Calibration:	Na ⁺ , Cu ⁺ , Cu ₂ OH ⁺ , Cu ₃ O ⁺ , ⁶⁵ CuCu ₃ O ₂ ⁺ , ⁶⁵ CuCu ₄ O ₂ ⁺
Specimen Normal-to-Analyzer:	0°
Source-to-Analyzer Angle:	45°
Primary Beam Ion Gun:	LMIG
Primary Ion Species:	Bi ₃ ⁺
Primary Ion Dose:	4.35 × 10 ¹¹ ion/cm ²
Primary Ion Pulse Width:	0.8–1.2 ns
Primary Ion Pulse Rate:	5 kHz
Net Beam Voltage:	25 000 eV
Pulsed Beam Current:	0.000 13 nA
DC Beam Current:	10.4 nA
Beam Diameter:	~2 μm
Beam Raster Size:	250 × 250 μm ²
Beam Incident Angle:	45°
Secondary Source Polarity:	Positive
Mass Range Minimum:	0 Da
Mass Range Maximum:	3545 Da
Spectrum Dead Time Corrected:	Yes
Total Spectral Acquisition Time:	335 s
Comment:	Organic contamination, likely from pigment processing. ⁸ Additional series of peaks are detected, with lower intensity. Some can be attributed to Cu _n O ₄ ⁺ with n = 7–8. Other can be attributed to Ba _n O _n H ⁺ with n = 3–4 from Ba-rich impurities.

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SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01944-01	22.990 (29.8)	Na ⁺	–
	26.981 (–4.25)	Al ⁺	–
	38.964 (26.9)	K ⁺	–
	62.928 (–18.0)	Cu ⁺	CuCO ₃ ·Cu(OH) ₂
	79.958 (26.4)	CuNH ₃ ⁺	–
	90.929 (–11.2)	CuC ₂ H ₄ ⁺	CuCO ₃ ·Cu(OH) ₂
	106.916 (–25.9)	CO ₂ Cu ⁺	CuCO ₃ ·Cu(OH) ₂
	125.857 (–15.3)	Cu ₂ ⁺	CuCO ₃ ·Cu(OH) ₂
	141.852 (–9.92)	Cu ₂ O ⁺	CuCO ₃ ·Cu(OH) ₂
	160.829 (8.01)	Cu ₂ Cl ⁺	–
	188.787 (–8.78)	Cu ₃ ⁺	CuCO ₃ ·Cu(OH) ₂
	204.781 (–11.5)	Cu ₃ O ⁺	CuCO ₃ ·Cu(OH) ₂
	220.775 (–16.1)	Cu ₃ O ₂ ⁺	CuCO ₃ ·Cu(OH) ₂
	264.757 (–42.9)	Cu ₃ O ₂ CO ₂ ⁺	CuCO ₃ ·Cu(OH) ₂
	283.704 (–13.0)	Cu ₄ O ₂ ⁺	CuCO ₃ ·Cu(OH) ₂
	302.685 (11.3)	Cu ₄ OCi ⁺	–
	314.647 (–1.96)	Cu ₅ ⁺	CuCO ₃ ·Cu(OH) ₂
	330.638 (–12.6)	Cu ₅ O ⁺	CuCO ₃ ·Cu(OH) ₂
	346.628 (–27.3)	Cu ₅ O ₂ ⁺	CuCO ₃ ·Cu(OH) ₂
	362.624 (–21.8)	Cu ₅ O ₃ ⁺	CuCO ₃ ·Cu(OH) ₂
	425.555 (–16.9)	Cu ₆ O ₃ ⁺	CuCO ₃ ·Cu(OH) ₂

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Accession #:	01944-01
■ Specimen:	Malachite, natural—Kremer Pigmente Ref. 10300
■ Technique:	SIMS
Instrument:	IONTOF, TOF SIMS IV
Analyzer Type:	Time-of-flight
Analyzer Mass Resolving Power:	2100 m/Δm
Mass Resolving Power Determined at:	27 Da
Species Used for Mass Calibration:	Na ⁺ , Cu ⁺ , Cu ₂ OH ⁺ , Cu ₃ O ⁺ , ⁶⁵ CuCu ₃ O ₂ ⁺ , ⁶⁵ CuCu ₄ O ₂ ⁺
Specimen Normal-to-Analyzer:	0°
Source-to-Analyzer Angle:	45°
Primary Beam Ion Gun:	LMIG
Primary Ion Species:	Bi ₃ ⁺
Primary Ion Dose:	4.35 × 10 ¹¹ ion/cm ²
Primary Ion Pulse Width:	0.8–1.2 ns
Primary Ion Pulse Rate:	5 kHz
Net Beam Voltage:	25 000 eV
Pulsed Beam Current:	0.000 13 nA
DC Beam Current:	10.4 nA
Beam Diameter:	~2 μm
Beam Raster Size:	250 × 250 μm
Beam Incident Angle:	45°
Secondary Source Polarity:	Positive
Mass Range Minimum:	0 Da
Mass Range Maximum:	3545 Da
Spectrum Dead Time Corrected:	Yes
Total Spectral Acquisition Time:	335 s
Comment:	Additional series of peaks are commonly detected in this compound, with lower intensity. They can be attributed to other Cu _x O _y ⁺ .

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SPECTRAL FEATURES TABLE

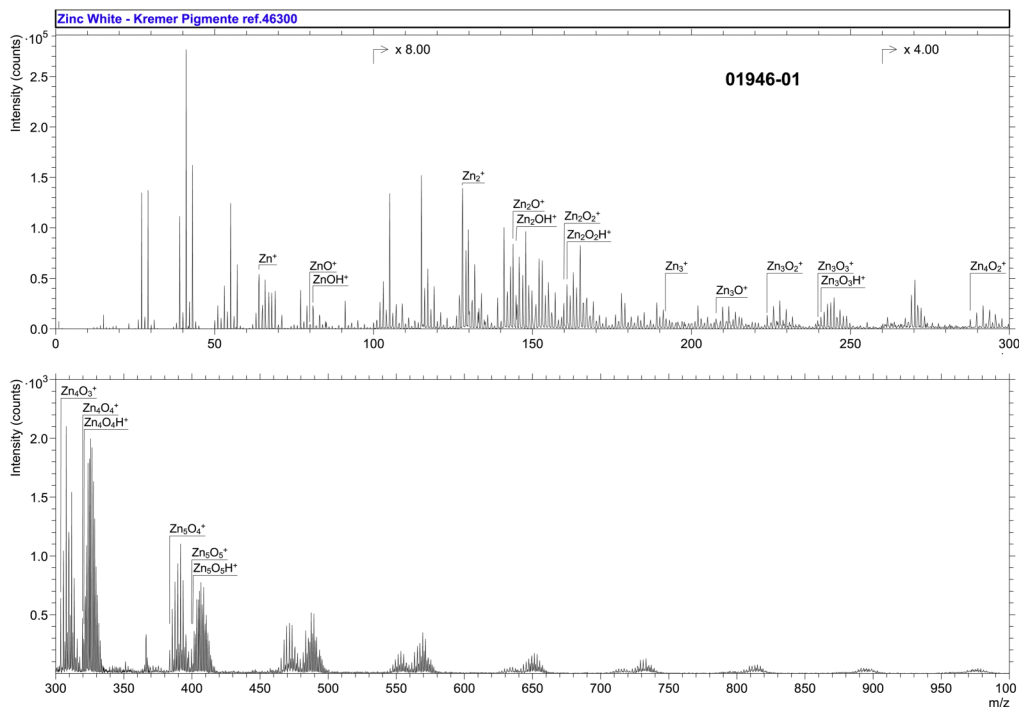
Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01945-01	15.023 (-24.0)	CH ₃ ⁺	Cu(CH ₃ COO) ₂
	43.017 (-18.3)	C ₂ H ₃ O ⁺	Cu(CH ₃ COO) ₂
	62.931 (29.0)	Cu ⁺	Cu(CH ₃ COO) ₂ ·[Cu(OH) ₂] ₃ ·2H ₂ O
	77.956 (47.4)	CH ₃ Cu ⁺	Cu(CH ₃ COO) ₂
	80.941 (17.0)	CuOH ₂ ⁺	Cu(CH ₃ COO) ₂ ·[Cu(OH) ₂] ₃ ·2H ₂ O
	88.943 (-15.0)	CuC ₂ H ₂ ⁺	Cu(CH ₃ COO) ₂
	90.924 (-0.84)	CuCO ⁺	Cu(CH ₃ COO) ₂
	104.938 (-14.8)	CuC ₂ H ₂ O ⁺	Cu(CH ₃ COO) ₂
	106.920 (11.2)	CuCO ₂ ⁺	Cu(CH ₃ COO) ₂
	122.949 (-10.4)	CuC ₂ H ₄ O ₂ ⁺	Cu(CH ₃ COO) ₂
	125.857 (-10.2)	Cu ₂ ⁺	Cu(CH ₃ COO) ₂ ·[Cu(OH) ₂] ₃ ·2H ₂ O
	140.882 (-3.47)	CH ₃ Cu ₂ ⁺	Cu(CH ₃ COO) ₂
	142.865 (22.0)	Cu ₂ OH ⁺	Cu(CH ₃ COO) ₂ ·[Cu(OH) ₂] ₃ ·2H ₂ O
	150.866 (-6.44)	Cu ₂ C ₂ H ⁺	Cu(CH ₃ COO) ₂
	166.863 (6.76)	Cu ₂ C ₂ OH ⁺	Cu(CH ₃ COO) ₂
	184.873 (5.96)	Cu ₂ C ₂ H ₃ O ₂ ⁺	Cu(CH ₃ COO) ₂
	188.788 (0.93)	Cu ₃ ⁺	Cu(CH ₃ COO) ₂ ·[Cu(OH) ₂] ₃ ·2H ₂ O
	204.786 (15.5)	Cu ₃ O ⁺	Cu(CH ₃ COO) ₂ ·[Cu(OH) ₂] ₃ ·2H ₂ O
	212.787 (-4.56)	Cu ₃ C ₂ ⁺	Cu(CH ₃ COO) ₂
	222.796 (-8.43)	Cu ₃ O ₂ H ₂ ⁺	Cu(CH ₃ COO) ₂ ·[Cu(OH) ₂] ₃ ·2H ₂ O
	228.786 (13.8)	Cu ₃ C ₂ O ⁺	Cu(CH ₃ COO) ₂
	243.897 (47.9)	Cu ₂ C ₄ H ₆ O ₄ ⁺	Cu(CH ₃ COO) ₂
	264.759 (-35.2)	Cu ₃ O ₂ CO ₂ ⁺	Cu(CH ₃ COO) ₂
	264.813 (32.1)	Cu ₃ OC ₂ H ₄ O ₂ ⁺	Cu(CH ₃ COO) ₂ ·[Cu(OH) ₂] ₃ ·2H ₂ O
	283.710 (8.67)	Cu ₄ O ₂ ⁺	Cu(CH ₃ COO) ₂ ·[Cu(OH) ₂] ₃ ·2H ₂ O
	284.718 (8.98)	Cu ₄ O ₂ H ⁺	Cu(CH ₃ COO) ₂ ·[Cu(OH) ₂] ₃ ·2H ₂ O
	292.718 (-8.63)	Cu ₄ C ₂ OH ⁺	Cu(CH ₃ COO) ₂
	306.810 (-17.3)	Cu ₃ C ₄ H ₆ O ₄ ⁺	Cu(CH ₃ COO) ₂
	323.811 (-20.7)	Cu ₃ C ₄ H ₇ O ₅ ⁺	Cu(CH ₃ COO) ₂
	326.718 (-25.8)	Cu ₄ OC ₂ H ₃ O ₂ ⁺	Cu(CH ₃ COO) ₂
	330.641 (-3.33)	Cu ₅ O ⁺	Cu(CH ₃ COO) ₂ ·[Cu(OH) ₂] ₃ ·2H ₂ O
	346.631 (-17.0)	Cu ₅ O ₂ ⁺	Cu(CH ₃ COO) ₂ ·[Cu(OH) ₂] ₃ ·2H ₂ O
	365.821 (-20.0)	Cu ₃ C ₆ H ₉ O ₆ ⁺	Cu(CH ₃ COO) ₂
	381.817 (-16.7)	Cu ₃ OC ₆ H ₉ O ₆ ⁺	Cu(CH ₃ COO) ₂
	406.646 (-30.6)	Cu ₅ C ₂ H ₄ O ₄ ⁺	Cu(CH ₃ COO) ₂
	424.834 (-17.5)	Cu ₃ C ₈ H ₁₂ O ₈ ⁺	Cu(CH ₃ COO) ₂
	428.753 (-10.7)	Cu ₄ C ₆ H ₉ O ₆ ⁺	Cu(CH ₃ COO) ₂
	448.663 (-12.5)	Cu ₅ OC ₄ H ₆ O ₄ ⁺	Cu(CH ₃ COO) ₂
	483.840 (-31.6)	Cu ₃ C ₁₀ H ₁₅ O ₁₀ ⁺	Cu(CH ₃ COO) ₂
	503.752 (-28.6)	Cu ₄ OC ₈ H ₁₂ O ₈ ⁺	Cu(CH ₃ COO) ₂
570.615 (5.87)	Cu ₆ OC ₆ H ₉ O ₆ ⁺	Cu(CH ₃ COO) ₂	
696.504 (47.0)	Cu ₈ OC ₆ H ₉ O ₆ ⁺	Cu(CH ₃ COO) ₂	

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SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01946-01	63.928 (-4.74)	Zn ⁺	ZnO
	79.926 (24.9)	ZnO ⁺	ZnO
	80.934 (33.0)	ZnOH ⁺	ZnO
	127.858 (3.66)	Zn ₂ ⁺	ZnO
	143.854 (9.57)	Zn(ZnO) ⁺	ZnO
	144.861 (4.73)	Zn(ZnOH) ⁺	ZnO
	159.849 (9.94)	(ZnO) ₂ ⁺	ZnO
	160.857 (12.0)	(ZnO) ₂ H ⁺	ZnO
	191.789 (8.58)	Zn ₃ ⁺	ZnO
	207.783 (6.72)	Zn ₃ O ⁺	ZnO
	223.777 (1.53)	Zn(ZnO) ₂ ⁺	ZnO
	239.772 (-0.48)	(ZnO) ₃ ⁺	ZnO
	240.779 (-2.54)	(ZnO) ₃ H ⁺	ZnO
	287.708 (7.95)	Zn ₄ O ₂ ⁺	ZnO
	303.697 (-11.3)	Zn(ZnO) ₃ ⁺	ZnO
	319.690 (-16.7)	(ZnO) ₄ ⁺	ZnO
	320.701 (-9.34)	(ZnO) ₄ H ⁺	ZnO
	383.627 (6.36)	Zn(ZnO) ₄ ⁺	ZnO
	399.622 (6.27)	(ZnO) ₅ ⁺	ZnO
	400.634 (16.0)	(ZnO) ₅ H ⁺	ZnO

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Accession #:

01946-01

■ Specimen:

Zinc White—Kremer Pigmente Ref. 46300

■ Technique:

SIMS

Instrument:

IONTOF, TOF SIMS IV

Analyzer Type:

Time-of-flight

Analyzer Mass Resolving Power:

4200 m/Δm

Mass Resolving Power Determined at:

27 Da

Species Used for Mass Calibration:

Na⁺, Zn⁺, Zn₂O₂⁺, Zn₃O₃⁺, ⁶⁶Zn⁶⁸ZnZn₂O₄⁺, ⁶⁶Zn⁶⁸ZnZn₃O₅⁺

Specimen Normal-to-Analyzer:

0°

Source-to-Analyzer Angle:

45°

Primary Beam Ion Gun:

LMIG

Primary Ion Species:

Bi₃⁺

Primary Ion Dose:

4.37 × 10¹¹ ion/cm²

Primary Ion Pulse Width:

0.8–1.2 ns

Primary Ion Pulse Rate:

5 kHz

Net Beam Voltage:

25 000 eV

Pulsed Beam Current:

0.000 15 nA

DC Beam Current:

14.7 nA

Beam Diameter:

~2 μm

Beam Raster Size:

250 × 250 μm²

Beam Incident Angle:

45°

Secondary Source Polarity:

Positive

Mass Range Minimum:

0 Da

Mass Range Maximum:

3545 Da

Spectrum Dead Time Corrected:

Yes

Total Spectral Acquisition Time:

293 s

Comment:

Distinctive isotopic pattern for Zn. Exogenous organic contamination. Peaks attributed to (ZnO)_x⁺ are commonly present up to x = 9, with lower intensity.

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