



HAL
open science

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

Caroline Bouvier, Sebastiaan van Nuffel, Alain Brunelle

► **To cite this version:**

Caroline Bouvier, Sebastiaan van Nuffel, Alain Brunelle. Tof-SIMS spectra of historical inorganic pigments: Copper-, zinc-, arsenic-, and phosphorus-containing pigments in negative polarity. *Surface Science Spectra*, 2024, 31 (2), pp.025002. 10.1116/6.0003723 . hal-04644238

HAL Id: hal-04644238

<https://hal.science/hal-04644238v1>

Submitted on 10 Jul 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

RESEARCH ARTICLE | JULY 10 2024

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

Caroline Bouvier  ; Sebastiaan Van Nuffel  ; Alain Brunelle  



Surf. Sci. Spectra 31, 025002 (2024)

<https://doi.org/10.1116/6.0003723>



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

Cite as: Surf. Sci. Spectra **31**, 025002 (2024); doi: [10.1116/6.0003723](https://doi.org/10.1116/6.0003723)

Submitted: 27 April 2024 · Accepted: 18 June 2024 ·

Published Online: 10 July 2024



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

Note: This paper is part of the 2024 Special Topic Collection on ToF-SIMS Spectra of Historical Inorganic Pigments.

^{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 negative 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.

© 2024 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>). <https://doi.org/10.1116/6.0003723>

Accession#: 01947, 01948, 01949, 01950, 01951, 01952, 01953, and 01954

Technique: SIMS

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

Instrument: IONTOF, TOF SIMS IV

Major Species in Spectra: O, H, C, Cu, Zn, P, Ca, As, S, V, Bi, and 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. Although not presented in the paper, titanium oxide, used as a pigment from the 1920s, may exhibit additional interferences to be considered as TiO^- has an m/z of 62.94.

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,

10 July 2024 19:07:58

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.

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 a 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 a 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 (#01949), 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 of 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. 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. Copper and zinc both have distinctive isotopic patterns ensuring confident attribution of the peaks, so #01951, #01952, and #01953 data were calibrated using lists including Cu⁻ and Cu₃O₃⁻ ions, and #01954 data were calibrated using ZnO₂⁻, Zn₂O₃⁻, Zn₃O₄⁻, ⁶⁶Zn⁶⁸ZnZn₂O₆⁻, ⁶⁶Zn⁶⁸Zn₂Zn₄O₈⁻, and ⁶⁶Zn⁶⁸Zn₂Zn₅O₁₀⁻. When possible, data were calibrated using lists including main ions, namely, C⁻, C₂⁻, C₃⁻, C₈⁻, C₁₀⁻, and C₁₃⁻ for #01947, CaO⁻, SiO₂⁻, PO₂⁻, SiO₃⁻, and PO₃⁻ for #01948, and S₂⁻, AsS₂⁻, As₂S₃⁻, and As₃S₄⁻ for #01949. No bismuth- and vanadium-containing ions were used to calibrate the #01950 dataset since bismuth has no isotope and is close in mass to VP₂O₆. Hence, #01950 data were calibrated using hydrocarbon and chlorine ions CH⁻, CH₂⁻, C₂⁻, Cl⁻, C₃⁻, and C₄H⁻. 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. 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 negative 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 current literature.^{2–6} The spectrum ID# refers to that number.

SPECIMEN DESCRIPTION (ACCESSION # 01947)

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-base 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 a 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 of 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: Ar_{1500–2000}, 20 keV, 2×10^{15} ions/cm²

SPECIMEN DESCRIPTION (ACCESSION # 01948)

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 and calcium phosphates

Form: Ground pigment powder

10 JULY 2024 19:07:58

History and Significance: Bone black is made by carbonization of animal bones at temperatures over 400 °C but not above 800 °C. It mainly consists of calcium phosphate and carbonized 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 a 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 of 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 # 01949)

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, its geographic origin varies. It was found on 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 of 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 # 01950)

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

CAS Registry #: 7779-90-0 and 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 a 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 of 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 # 01951)

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.

10 July 2024 19:07:58

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 a 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 of 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, 2×10^{15} ions/ cm^2

SPECIMEN DESCRIPTION (ACCESSION # 01952)

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 a 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 of 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, 2×10^{15} ions/ cm^2

SPECIMEN DESCRIPTION (ACCESSION # 01953)

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 in 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 a 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 of 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, 2×10^{15} ions/ cm^2

SPECIMEN DESCRIPTION (ACCESSION # 01954)

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 a 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 of 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: 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: Bi₃⁺

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 μ m

Beam Raster Size: 250 \times 250 μ m²

Raster Pixel Dimensions: 128 \times 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 gas cluster ion beam (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 μ m

Beam Raster Size: 500 \times 500 μ m²

Raster Pixel Dimensions: N/A

Beam Incident Angle: 45°

Source-to-Analyzer Angle: 45°

ACKNOWLEDGMENTS

This work was financially supported by the Agence Nationale de la Recherche (Grant No. ANR-2015-CE29-0007 DEFIMAGE). C.B. has received funding from the European Union’s Horizon Europe Research and Innovation Programme under the Marie Skłodowska-Curie Grant Agreement No 101108506. The authors thank Sven Kayser and Matthias Kleine-Boymann (IONTOF GmbH) for providing extended access to software SurfaceLab 7.3 that allowed thorough processing of the data.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Caroline Bouvier: Investigation (lead); Writing – original draft (lead). **Sebastian 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.

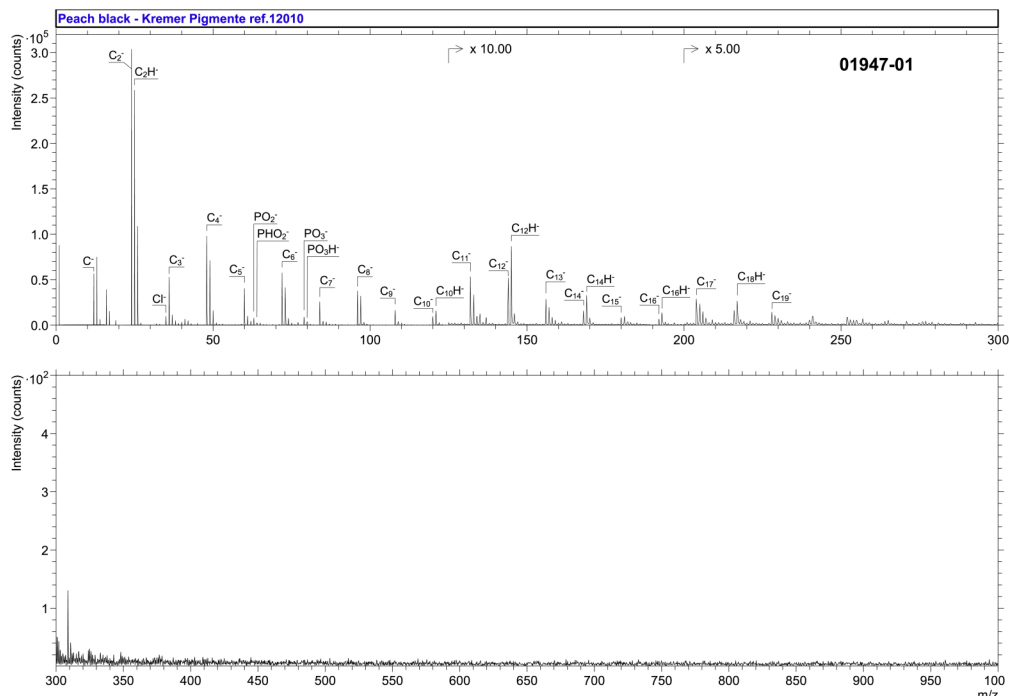
REFERENCES

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

SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01947-01	12.000 (-3.10)	C ⁻	Charcoal
	24.000 (-18.7)	C ₂ ⁻	Charcoal
	25.008 (-2.87)	C ₂ H ⁻	Charcoal
	34.969 (-10.7)	Cl ⁻	—
	36.000 (-17.2)	C ₃ ⁻	Charcoal
	47.999 (-26.4)	C ₄ ⁻	Charcoal
	60.001 (8.18)	C ₅ ⁻	Charcoal
	62.966 (27.8)	PO ₂ ⁻	—
	63.972 (0.44)	HPO ₂ ⁻	—
	72.002 (17.1)	C ₆ ⁻	Charcoal
	78.962 (40.2)	PO ₃ ⁻	—
	79.967 (2.85)	HPO ₃ ⁻	—
	84.001 (3.17)	C ₇ ⁻	Charcoal
	96.000 (-15.0)	C ₈ ⁻	Charcoal
	107.999 (-15.4)	C ₉ ⁻	Charcoal
	119.998 (-19.0)	C ₁₀ ⁻	Charcoal
	121.009 (5.26)	HC ₁₀ ⁻	Charcoal
	131.998 (-19.3)	C ₁₁ ⁻	Charcoal
	143.998 (-16.1)	C ₁₂ ⁻	Charcoal
	145.009 (5.84)	HC ₁₂ ⁻	Charcoal
155.999 (-12.8)	C ₁₃ ⁻	Charcoal	
167.997 (-20.2)	C ₁₄ ⁻	Charcoal	
169.010 (10.2)	HC ₁₄ ⁻	Charcoal	
179.998 (-12.5)	C ₁₅ ⁻	Charcoal	
191.996 (-23.4)	C ₁₆ ⁻	Charcoal	
193.007 (-9.01)	C ₁₆ H ⁻	Charcoal	
203.994 (-34.1)	C ₁₇ ⁻	Charcoal	
217.009 (-34.3)	C ₁₈ H ⁻	Charcoal	
227.995 (-26.6)	C ₁₉ ⁻	Charcoal	

10 July 2024 19:07:58



Accession #:

01947-01

<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 1700 m/Δm 25 Da C^-, C_2^-, C_3^-, C_8^-, C_{10}^-, and C_{13}^- 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 ~2 μm 250 × 250 μm² 45° Negative 0 Da 3545 Da Yes 335 s </p>
---	--

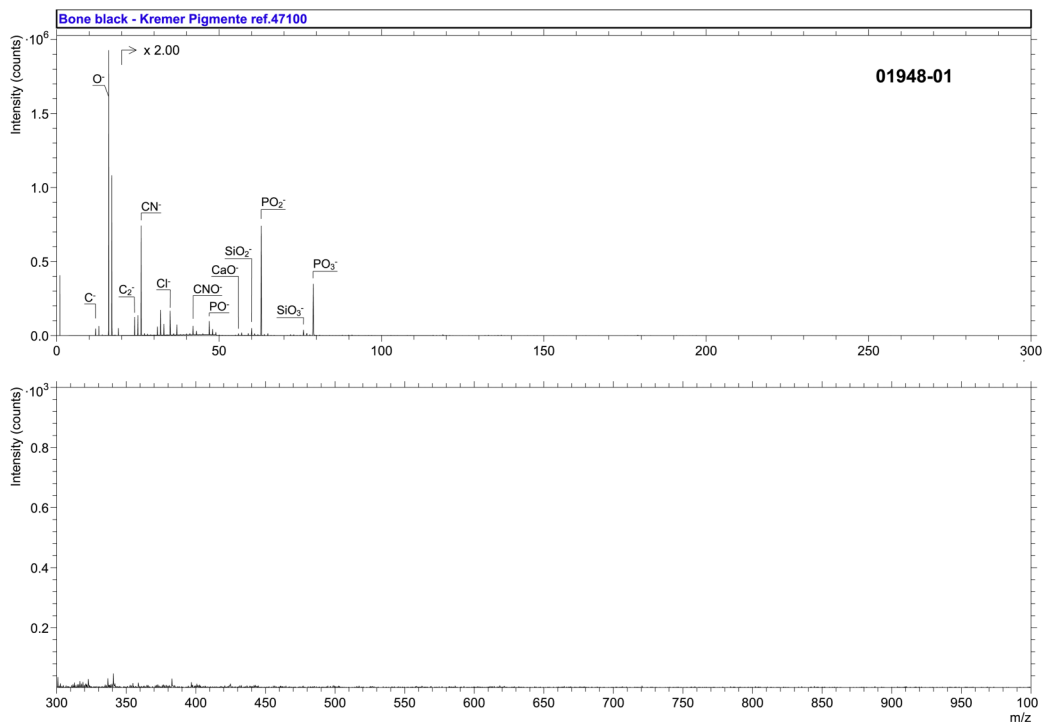
TOF-SIMS can be used to characterize carbon-based pigments. Both C_n^- and HC_n^- are detected until $n = 20$, even if only the higher ones are labelled on the figure.

10 July 2024 19:07:58

SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01948-01	12.001 (27.4)	C ⁻	Charred material
	15.996 (31.0)	O ⁻	—
	24.001 (21.4)	C ₂ ⁻	Charred material
	26.004 (20.2)	CN ⁻	Possible protein residue
	34.970 (2.50)	Cl ⁻	—
	41.999 (16.9)	CNO ⁻	Possible protein residue
	46.969 (-3.76)	PO ⁻	Calcium phosphate
	55.957 (-14.8)	CaO ⁻	Calcium phosphate
	59.966 (-25.1)	SiO ₂ ⁻	Aluminosilicate
	62.964 (3.05)	PO ₂ ⁻	Calcium phosphate
	75.964 (20.2)	SiO ₃ ⁻	Aluminosilicate
	78.961 (17.9)	PO ₃ ⁻	Calcium phosphate

10 July 2024 19:07:58



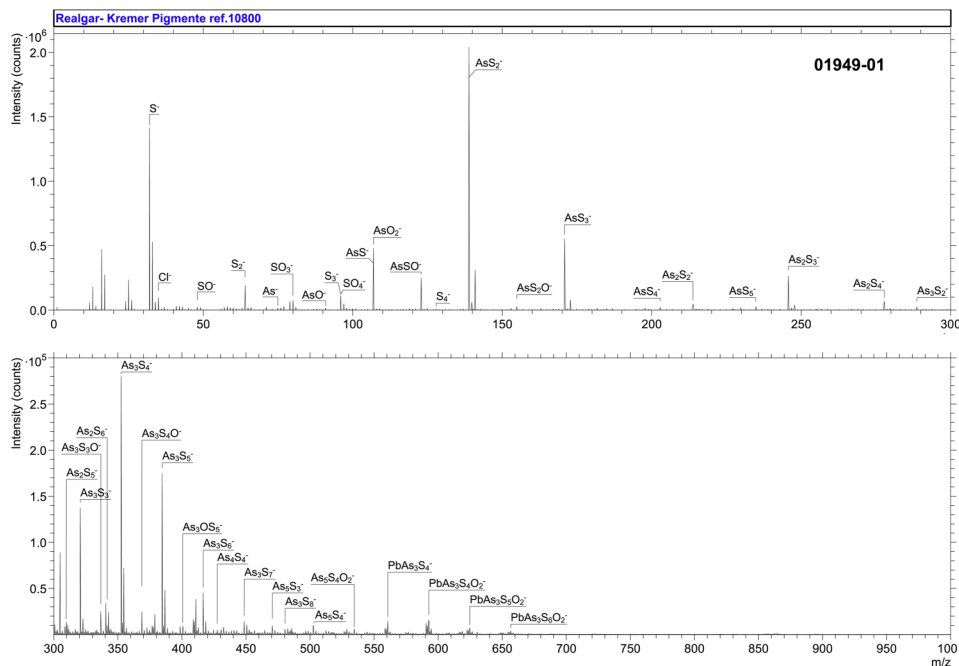
Accession #:	01948-01
■ Specimen:	Bone Black—Kremer Pigmente Ref. 47100
■ Technique:	SIMS
Instrument:	IONTOF, TOF SIMS IV
Analyzer Type:	Time of flight
Analyzer Mass Resolving Power:	3000 m/Δm
Mass Resolving Power Determined at:	25 Da
Species Used for Mass Calibration:	O ⁻ , CaO ⁻ , SiO ₂ ⁻ , PO ₂ ⁻ , SiO ₃ ⁻ , and PO ₃ ⁻
Specimen Normal-to-Analyzer:	0°
Source-to-Analyzer Angle:	45°
Primary Beam Ion Gun:	LMIG
Primary Ion Species:	Bi ₃ ⁺
Primary Ion Dose:	4.37 × 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 15 nA
DC Beam Current:	14.7 nA
Beam Diameter:	~2 μm
Beam Raster Size:	250 × 250 μm ²
Beam Incident Angle:	45°
Secondary Source Polarity:	Negative
Mass Range Minimum:	0 Da
Mass Range Maximum:	3545 Da
Spectrum Dead Time Corrected:	Yes
Total Spectral Acquisition Time:	292 s
Comment:	Notable low signal intensity for carbon clusters C _n ⁻ compared to Peach black (#01947 up to n = 6, and no C _n ⁻ detection for n > 7).

10 July 2024 19:07:58

SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01949-01	31.973 (9.88)	S^-	α -As ₄ S ₄
	34.970 (21.7)	Cl^-	Natural impurity
	47.967 (-19.4)	SO^-	—
	63.946 (14.7)	S_2^-	α -As ₄ S ₄
	74.923 (14.6)	As^-	α -As ₄ S ₄
	79.960 (28.4)	SO_3^-	—
	90.915 (-21.5)	AsO^-	Arsenic oxide
	95.917 (3.55)	S_3^-	α -As ₄ S ₄
	95.953 (9.50)	SO_4^-	—
	106.891 (-25.6)	AsS^-	α -As ₄ S ₄
	106.914 (18.7)	AsO_2^-	Arsenic oxide
	122.890 (5.76)	$AsSO^-$	Arsenic oxide
	127.889 (0.58)	S_4^-	α -As ₄ S ₄
	138.868 (14.5)	AsS_2^-	α -As ₄ S ₄
	154.860 (-7.08)	AsS_2O^-	Arsenic oxide
	170.838 (-3.81)	AsS_3^-	α -As ₄ S ₄
	202.810 (-4.31)	AsS_4^-	α -As ₄ S ₄
	213.784 (-16.6)	$As_2S_2^-$	α -As ₄ S ₄
	234.781 (-6.40)	AsS_5^-	α -As ₄ S ₄
	245.756 (-14.1)	$As_2S_3^-$	α -As ₄ S ₄
	277.730 (-5.85)	$As_2S_4^-$	α -As ₄ S ₄
	288.710 (0.64)	$As_3S_2^-$	α -As ₄ S ₄
	309.704 (-1.19)	$As_2S_5^-$	α -As ₄ S ₄
	320.680 (-4.32)	$As_3S_3^-$	α -As ₄ S ₄
	336.681 (12.1)	$As_3S_3O^-$	Arsenic oxide
	341.673 (-9.75)	$As_2S_6^-$	α -As ₄ S ₄
	352.657 (10.3)	$As_3S_4^-$	α -As ₄ S ₄
	368.651 (6.43)	$As_3S_4O^-$	Arsenic oxide
	384.627 (2.52)	$As_3S_5^-$	α -As ₄ S ₄
	400.660 (11.8)	$As_3S_5O^-$	Arsenic oxide
	416.594 (-8.57)	$As_3S_6^-$	α -As ₄ S ₄
	427.561 (-33.1)	$As_4S_4^-$	α -As ₄ S ₄
	448.552 (-39.9)	$As_3S_7^-$	α -As ₄ S ₄
470.510 (-30.9)	$As_5S_3^-$	α -As ₄ S ₄	
480.523 (-38.9)	$As_3S_8^-$	α -As ₄ S ₄	
502.496 (-1.95)	$As_5S_4^-$	α -As ₄ S ₄	
534.481 (-10.4)	$As_5S_4O_2^-$	Arsenic oxide	
560.615 (-26.9)	$PbAs_3S_4^-$	Natural impurity	
592.624 (5.89)	$PbAs_3S_4O_2^-$	Natural impurity	
624.595 (5.15)	$PbAs_3S_5O_2^-$	Natural impurity	
656.560 (-6.62)	$PbAs_3S_6O_2^-$	Natural impurity	

10 July 2024 19:07:58



Accession #:

01949-01

<p>■ Specimen:</p> <p>■ Technique:</p> <p>Instrument:</p> <p>Analyzer Type:</p> <p>Analyzer Mass Resolving Power:</p> <p>Mass Resolving Power Determined at:</p> <p>Species Used for Mass Calibration:</p> <p>Specimen Normal-to-Analyzer:</p> <p>Source-to-Analyzer Angle:</p> <p>Primary Beam Ion Gun:</p> <p>Primary Ion Species:</p> <p>Primary Ion Dose:</p> <p>Primary Ion Pulse Width:</p> <p>Primary Ion Pulse Rate:</p> <p>Net Beam Voltage:</p> <p>Pulsed Beam Current:</p> <p>DC Beam Current:</p> <p>Beam Diameter:</p> <p>Beam Raster Size:</p> <p>Beam Incident Angle:</p> <p>Secondary Source Polarity:</p> <p>Mass Range Minimum:</p> <p>Mass Range Maximum:</p> <p>Spectrum Dead Time Corrected:</p> <p>Total Spectral Acquisition Time:</p> <p>Comment:</p>	<p>Realgar/red orpiment—Kremer Pigmente Ref. 10800</p> <p>SIMS</p> <p>IONTOF, TOF SIMS IV</p> <p>Time of flight</p> <p>3300 m/Δm</p> <p>25 Da</p> <p>OH^-, S_2^-, AsS_2^-, As_2S_3^-, and As_3S_4^-</p> <p>0°</p> <p>45°</p> <p>LMIG</p> <p>Bi_3^+</p> <p>4.34×10^{11} ion/cm²</p> <p>0.8–1.2 ns</p> <p>5 kHz</p> <p>25 000 eV</p> <p>0.000 21 nA</p> <p>14.4 nA</p> <p>$\sim 2 \mu\text{m}$</p> <p>$250 \times 250 \mu\text{m}^2$</p> <p>$45^\circ$</p> <p>Negative</p> <p>0 Da</p> <p>3545 Da</p> <p>Yes</p> <p>207 s</p>
---	---

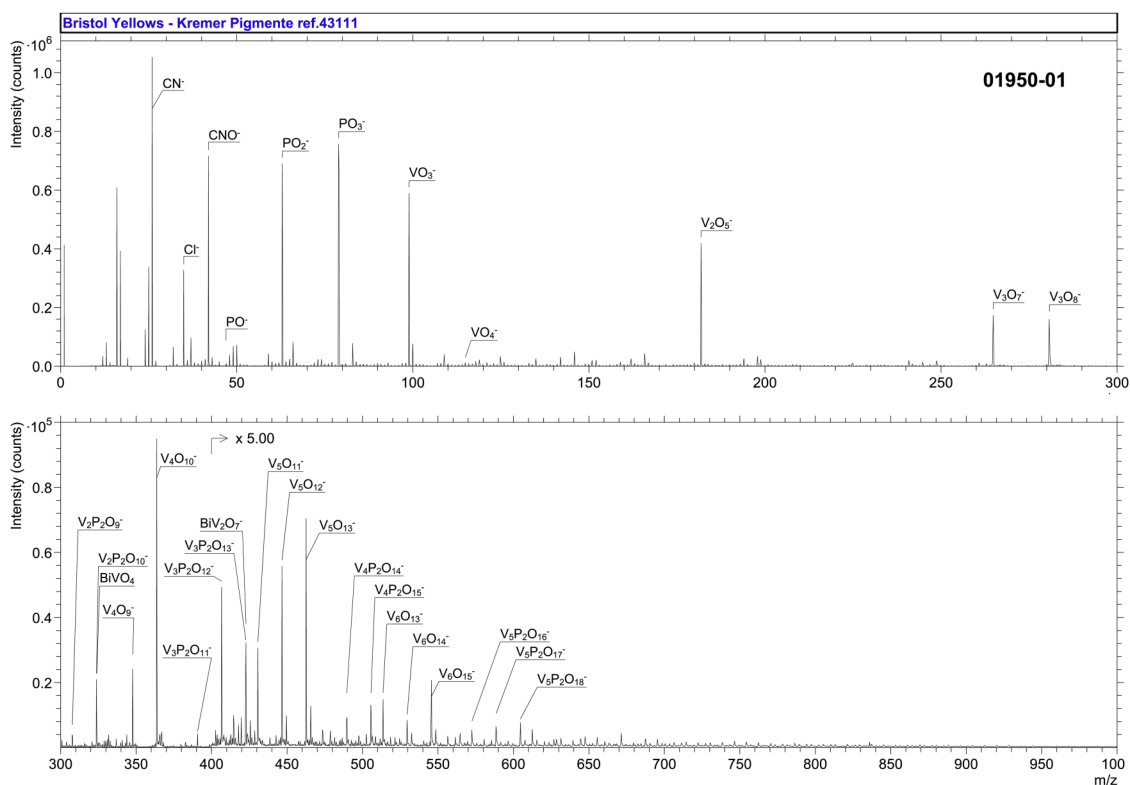
Unstable, sensitive to light and oxygen. All oxygen-containing ions were localized in round-shaped areas of about $10 \mu\text{m}$ diameter dispersed within the analyzed surface of $250 \times 250 \mu\text{m}^2$, allowing us to confidently determine whether a species contained oxygen or only sulfur.

10 July 2024 19:07:58

SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01950-01	26.004 (10.1)	CN ⁻	—
	42.000 (12.5)	CNO ⁻	—
	46.967 (-52.6)	PO ⁻	Zn ₃ (PO ₄) ₂
	62.965 (19.3)	PO ₂ ⁻	Zn ₃ (PO ₄) ₂
	78.961 (26.0)	PO ₃ ⁻	Zn ₃ (PO ₄) ₂
	98.929 (-3.86)	VO ₃ ⁻	BiVO ₄
	114.923 (6.57)	VO ₄ ⁻	BiVO ₄
	181.863 (-0.50)	V ₂ O ₅ ⁻	BiVO ₄
	264.796 (-1.62)	V ₃ O ₇ ⁻	BiVO ₄
	280.793 (6.97)	V ₃ O ₈ ⁻	BiVO ₄
	307.777 (-43.3)	V ₂ P ₂ O ₉ ⁻	Zn ₃ (PO ₄) ₂ + BiVO ₄
	323.772 (-40.7)	V ₂ P ₂ O ₁₀ ⁻	Zn ₃ (PO ₄) ₂ + BiVO ₄
	323.897 (-22.7)	BiVO ₄ ⁻	BiVO ₄
	347.732 (5.10)	V ₄ O ₉ ⁻	BiVO ₄
	363.730 (11.2)	V ₄ O ₁₀ ⁻	BiVO ₄
	390.704 (-50.8)	V ₃ P ₂ O ₁₁ ⁻	Zn ₃ (PO ₄) ₂ + BiVO ₄
	406.701 (-44.6)	V ₃ P ₂ O ₁₂ ⁻	Zn ₃ (PO ₄) ₂ + BiVO ₄
	422.690 (-56.6)	V ₃ P ₂ O ₁₃ ⁻	Zn ₃ (PO ₄) ₂ + BiVO ₄
	422.824 (-21.5)	BiV ₂ O ₇ ⁻	BiVO ₄
	430.660 (-9.62)	V ₅ O ₁₁ ⁻	BiVO ₄
	446.661 (3.97)	V ₅ O ₁₂ ⁻	BiVO ₄
	462.655 (1.43)	V ₅ O ₁₃ ⁻	BiVO ₄
	489.631 (-43.5)	V ₄ P ₂ O ₁₄ ⁻	Zn ₃ (PO ₄) ₂ + BiVO ₄
	505.641 (-13.7)	V ₄ P ₂ O ₁₅ ⁻	Zn ₃ (PO ₄) ₂ + BiVO ₄
	513.606 (15.6)	V ₆ O ₁₃ ⁻	BiVO ₄
	529.606 (23.9)	V ₆ O ₁₄ ⁻	BiVO ₄
	545.598 (17.9)	V ₆ O ₁₅ ⁻	BiVO ₄
	572.571 (-26.5)	V ₅ P ₂ O ₁₆ ⁻	Zn ₃ (PO ₄) ₂ + BiVO ₄
	588.592 (17.9)	V ₅ P ₂ O ₁₇ ⁻	Zn ₃ (PO ₄) ₂ + BiVO ₄
	604.593 (27.8)	V ₅ P ₂ O ₁₈ ⁻	Zn ₃ (PO ₄) ₂ + BiVO ₄

10 July 2024 19:07:58



Accession #:

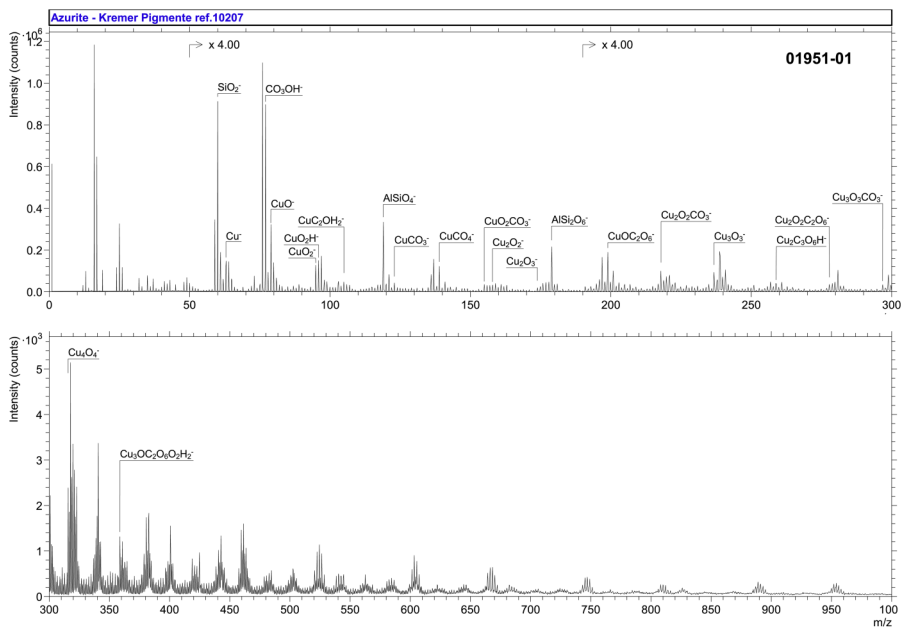
01950-01

<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:</p>	<p>Bristol Yellow—Kremer Pigmente Ref. 43111 SIMS IONTOF, TOF SIMS IV Time of flight 3500 m/Δm 25 Da CH⁻, CH₂⁻, C₂⁻, Cl⁻, C₃⁻, and C₄H⁻ 0° 45° LMIG Bi₃⁺ 4.35 × 10¹¹ ion/cm² 0.8–1.2 ns 5 kHz 25 000 eV 0.000 17 nA 15.1 nA ~2 μm 250 × 250 μm² 45° Negative 0 Da 3545 Da Yes 256 s</p>
---	--

10 July 2024 19:07:58

SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01951-01	62.931 (10.7)	Cu^-	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
	76.985 (-37.5)	CO_3OH^-	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
	78.925 (-0.79)	CuO^-	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
	94.919 (-11.5)	CuO_2^-	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
	95.930 (19.6)	CuO_2H^-	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
	104.947 (59.4)	$\text{CuC}_2\text{H}_2\text{O}^-$	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
	118.943 (33.2)	AlSiO_4^-	Aluminosilicate interference
	122.915 (-3.49)	CuCO_3^-	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
	138.909 (-7.33)	CuCO_4^-	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
	154.902 (-18.3)	$\text{CuO}_2\text{CO}_3^-$	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
	157.856 (39.9)	Cu_2O_2^-	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
	173.843 (-6.04)	Cu_2O_3^-	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
	178.913 (41.4)	$\text{Si}_2\text{AlO}_6^-$	Aluminosilicate interference
	198.887 (-38.4)	$\text{CuO}(\text{CO}_3)_2^-$	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
	217.835 (4.06)	$\text{Cu}_2\text{O}_2\text{CO}_3^-$	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
	236.772 (-7.29)	Cu_3O_3^-	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
	258.842 (20.5)	$\text{Cu}_2\text{C}_3\text{O}_6\text{H}^-$	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
	277.823 (14.6)	$\text{Cu}_2\text{O}_2(\text{CO}_3)_2^-$	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
	296.759 (-0.68)	$\text{Cu}_3\text{O}_3\text{CO}_3^-$	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
	315.700 (5.09)	Cu_4O_4^-	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
	358.764 (12.3)	$\text{Cu}_3\text{O}(\text{CO}_3)_2(\text{OH})_2^-$	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$



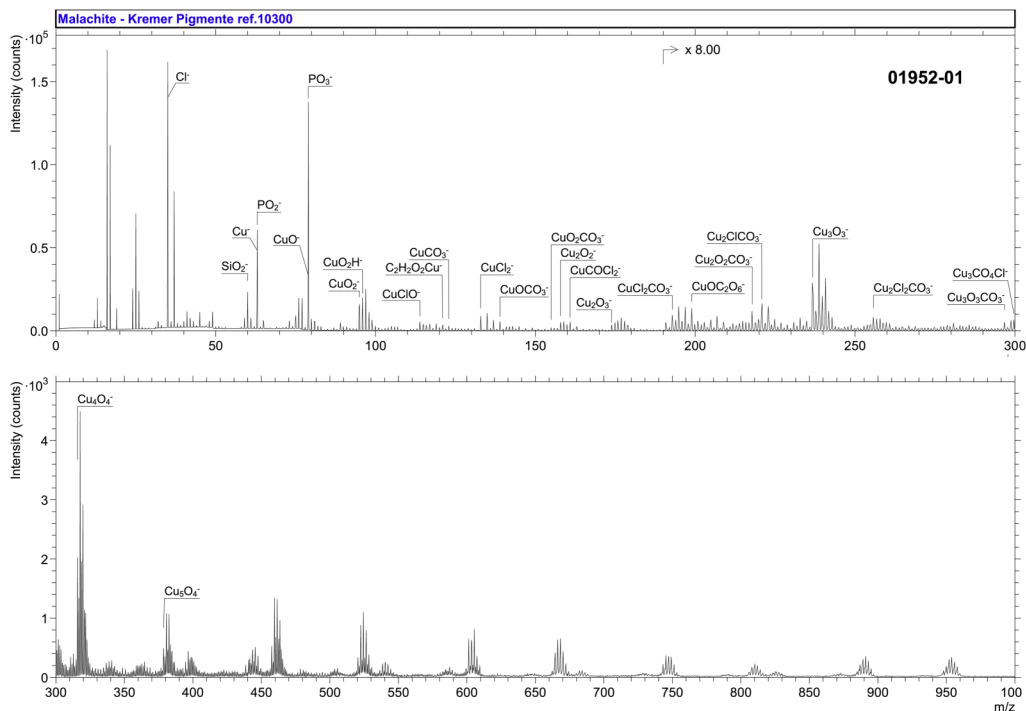
Accession #:	01951-01
■ Specimen:	Azurite—Kremer Pigmente Ref. 10207
■ Technique:	SIMS
Instrument:	IONTOF, TOF SIMS IV
Analyzer Type:	Time of flight
Analyzer Mass Resolving Power:	2000 m/Δm
Mass Resolving Power Determined at:	25 Da
Species Used for Mass Calibration:	Cl ⁻ , Cu ⁻ , CuO ₂ ⁻ , Cu ₃ O ₃ ⁻ , and Cu ₄ O ₄ ⁻
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:	Negative
Mass Range Minimum:	0 Da
Mass Range Maximum:	3545 Da
Spectrum Dead Time Corrected:	Yes
Total Spectral Acquisition Time:	335 s
Comment:	Aluminosilicates are also found in this sample, a possible impurity. Isotopic ratios for copper cluster ions are impacted by overlapping aluminosilicate ions. The peaks at m/z 59.97 and 75.97 are likely to be, respectively, CO ₃ ⁻ and CO ₄ ⁻ but also contain near isobaric interferences from, respectively, SiO ₂ ⁻ and SiO ₃ ⁻ . They are, therefore, not listed in the table. Additional series of peaks are commonly detected in this compound, with lower intensity. They can be attributed to other Cu _x O _y ⁻ .

10 July 2024 19:07:58

SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01952-01	34.970 (10.4)	Cl ⁻	—
	59.968 (7.61)	SiO ₂ ⁻	—
	62.930 (-7.31)	Cu ⁻	CuCO ₃ ·Cu(OH) ₂
	62.965 (6.21)	PO ₂ ⁻	—
	78.925 (-0.68)	CuO ⁻	CuCO ₃ ·Cu(OH) ₂
	78.963 (54.2)	PO ₃ ⁻	—
	94.921 (6.24)	CuO ₂ ⁻	CuCO ₃ ·Cu(OH) ₂
	95.929 (15.5)	CuO ₂ H ⁻	Cu ₃ (CO ₃) ₂ (OH) ₂
	104.945 (38.3)	Cu ₂ H ₂ O ⁻	CuCO ₃ ·Cu(OH) ₂
	113.896 (17.8)	CuOCl ⁻	—
	120.940 (35.9)	C ₂ H ₂ O ₂ Cu ⁻	CuCO ₃ ·Cu(OH) ₂
	122.918 (27.7)	CuCO ₃ ⁻	CuCO ₃ ·Cu(OH) ₂
	132.873 (39.9)	CuCl ₂ ⁻	—
	138.903 (-51.3)	CuCO ₄ ⁻	CuCO ₃ ·Cu(OH) ₂
	142.894 (-21.5)	CuHCO ₂ Cl ⁻	—
	154.901 (-27.4)	CuO ₂ CO ₃ ⁻	CuCO ₃ ·Cu(OH) ₂
	157.854 (25.1)	Cu ₂ O ₂ ⁻	CuCO ₃ ·Cu(OH) ₂
	160.867 (25.0)	CuCl ₂ CO ⁻	—
	173.847 (13.3)	Cu ₂ O ₃ ⁻	CuCO ₃ ·Cu(OH) ₂
	192.847 (-29.7)	CuCl ₂ CO ₃ ⁻	CuCO ₃ ·Cu(OH) ₂
	198.882 (-64.8)	Cu ₂ C ₂ O ₂ OH ⁻	CuCO ₃ ·Cu(OH) ₂
	211.799 (34.1)	Cu ₂ Cl ₂ O ⁻	—
	217.827 (-32.7)	Cu ₂ O ₂ CO ₃ ⁻	CuCO ₃ ·Cu(OH) ₂
	220.821 (34.2)	Cu ₂ ClCO ₃ ⁻	—
	236.774 (1.20)	Cu ₃ O ₃ ⁻	CuCO ₃ ·Cu(OH) ₂
	255.784 (5.09)	Cu ₂ Cl ₂ CO ₃ ⁻	—
	296.752 (-22.3)	Cu ₃ O ₃ CO ₃ ⁻	CuCO ₃ ·Cu(OH) ₂
	299.734 (-11.7)	Cu ₃ ClCO ₄ ⁻	—
	315.700 (5.68)	Cu ₄ O ₄ ⁻	CuCO ₃ ·Cu(OH) ₂
	378.635 (16.8)	Cu ₅ O ₄ ⁻	CuCO ₃ ·Cu(OH) ₂

10 July 2024 19:07:58



Accession #:

01952-01

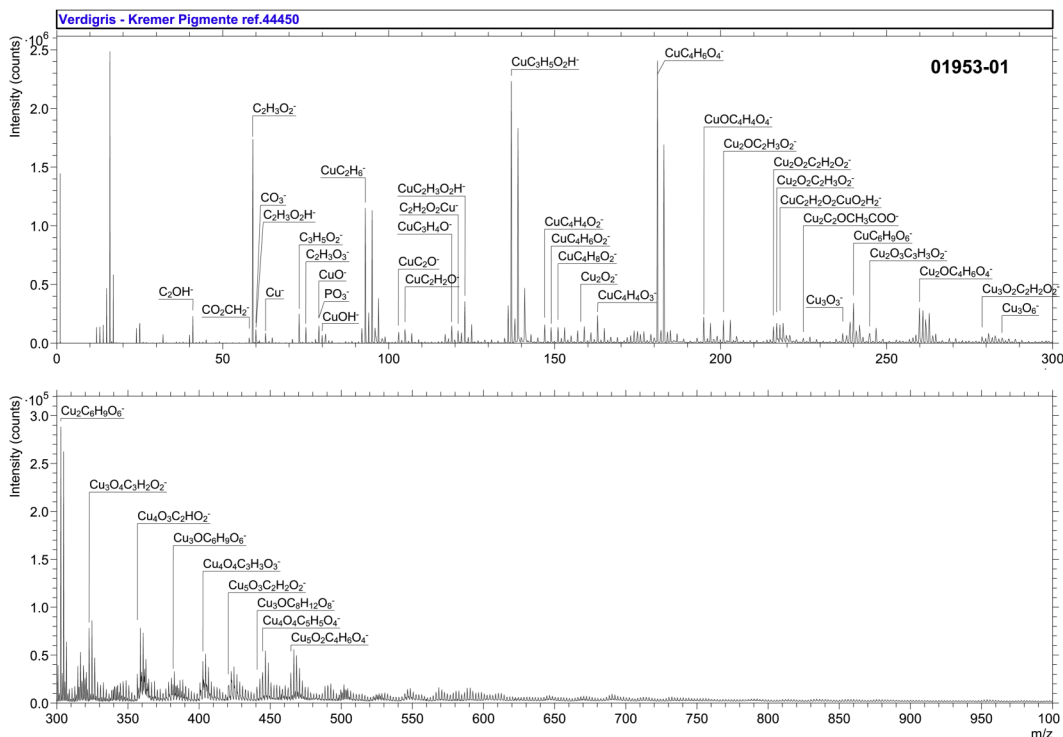
■ Specimen:	Malachite, natural—Kremer Pigmente Ref. 10300
■ Technique:	SIMS
Instrument:	IONTOF, TOF SIMS IV
Analyzer Type:	Time of flight
Analyzer Mass Resolving Power:	2000 m/ Δ m
Mass Resolving Power Determined at:	25 Da
Species Used for Mass Calibration:	Cl^- , Cu^- , CuO_2^- , Cu_3O_3^- , and Cu_4O_4^-
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:	0.00013 nA
DC Beam Current:	10.4 nA
Beam Diameter:	$\sim 2 \mu\text{m}$
Beam Raster Size:	$250 \times 250 \mu\text{m}^2$
Beam Incident Angle:	45°
Secondary Source Polarity:	Negative
Mass Range Minimum:	0 Da
Mass Range Maximum:	3545 Da
Spectrum Dead Time Corrected:	Yes
Total Spectral Acquisition Time:	355 s
Comment:	Chlorine is detected, as well as copper/chlorine cluster ions. Additional series of peaks are commonly detected in this compound, with lower intensity. They can be attributed to other Cu_xO_y^- .

10 July 2024 19:07:58

SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01953-01	41.004 (14.9)	C_2OH^-	$Cu(CH_3COO)_2$
	58.005 (-13.9)	$CO_2CH_2^-$	$Cu(CH_3COO)_2$
	59.017 (44.0)	$C_2H_3O_2^-$	$Cu(CH_3COO)_2$
	59.983 (-37.0)	CO_3^-	$Cu(CH_3COO)_2$
	60.019 (-40.7)	$C_2H_3O_2H^-$	$Cu(CH_3COO)_2$
	62.930 (-3.74)	Cu^-	$Cu(CH_3COO)_2 \cdot [Cu(OH)_2]_3 \cdot 2H_2O$
	73.033 (48.7)	$C_3H_5O_2^-$	$Cu(CH_3COO)_2$
	75.013 (60.0)	$C_2H_3O_3^-$	$Cu(CH_3COO)_2$
	77.954 (0.64)	$CuCH_3^-$	$Cu(CH_3COO)_2$
	78.922 (-37.1)	CuO^-	$Cu(CH_3COO)_2 \cdot [Cu(OH)_2]_3 \cdot 2H_2O$
	78.961 (20.1)	PO_3^-	—
	92.981 (40.5)	$CuC_2H_6^-$	$Cu(CH_3COO)_2$
	102.921 (-43.5)	CuC_2O^-	$Cu(CH_3COO)_2$
	104.944 (32.2)	$CuC_2H_2O^-$	$Cu(CH_3COO)_2$
	118.954 (-20.0)	$CuC_3H_4O^-$	$Cu(CH_3COO)_2$
	120.939 (28.9)	$C_2H_2O_2Cu^-$	$Cu(CH_3COO)_2$
	122.951 (-2.71)	$CuC_2H_3O_2H^-$	$Cu(CH_3COO)_2$
	136.972 (38.8)	$CuC_3H_5O_2H^-$	$Cu(CH_3COO)_2$
	146.951 (-2.73)	$CuC_4H_4O_2^-$	$Cu(CH_3COO)_2$
	148.962 (-35.5)	$CuC_4H_6O_2^-$	$Cu(CH_3COO)_2$
	150.980 (-20.6)	$CuC_4H_8O_2^-$	$Cu(CH_3COO)_2$
	157.851 (8.73)	$Cu_2O_2^-$	$Cu(CH_3COO)_2 \cdot [Cu(OH)_2]_3 \cdot 2H_2O$
	162.947 (7.60)	$CuC_4H_3O_2OH^-$	$Cu(CH_3COO)_2$
	180.962 (27.1)	$CuC_4H_6O_4^-$	$Cu(CH_3COO)_2$
	194.942 (30.2)	$CuOC_4H_4O_4^-$	$Cu(CH_3COO)_2$
	200.871 (17.2)	$Cu_2OC_2H_3O_2^-$	$Cu(CH_3COO)_2$
	215.863 (36.0)	$Cu_2O_2C_2H_2O_2^-$	$Cu(CH_3COO)_2$
	216.871 (35.2)	$Cu_2O_2C_2H_3O_2^-$	$Cu(CH_3COO)_2$
	217.866 (-20.5)	$CuC_2H_2O_2CuO_2H_2^-$	$Cu(CH_3COO)_2$
	224.860 (-36.3)	$Cu_2C_2OCH_3COO^-$	$Cu(CH_3COO)_2$
	236.778 (17.7)	$Cu_3O_3^-$	$Cu(CH_3COO)_2 \cdot [Cu(OH)_2]_3 \cdot 2H_2O$
	239.958 (-49.4)	$Cu_6H_9O_6^-$	$Cu(CH_3COO)_2$
	244.855 (-9.60)	$Cu_2O_3C_3H_3O_2^-$	$Cu(CH_3COO)_2$
	259.869 (-47.0)	$Cu_2OC_4H_6O_4^-$	$Cu(CH_3COO)_2$
	278.788 (12.1)	$Cu_3O_2C_2H_2O_2^-$	$Cu(CH_3COO)_2$
	284.760 (1.94)	$Cu_3O_6^-$	$Cu(CH_3COO)_2 \cdot [Cu(OH)_2]_3 \cdot 2H_2O$
	302.885 (-49.6)	$Cu_2C_6H_9O_6^-$	$Cu(CH_3COO)_2$
	322.776 (3.07)	$Cu_3O_4C_3H_2O_2^-$	$Cu(CH_3COO)_2$
	356.718 (46.2)	$Cu_4O_3C_2HO_2^-$	$Cu(CH_3COO)_2$
	381.810 (-37.8)	$Cu_3OC_6H_9O_6^-$	$Cu(CH_3COO)_2$
	402.710 (8.67)	$Cu_4O_4C_3H_3O_3^-$	$Cu(CH_3COO)_2$
	420.633 (-14.9)	$Cu_5O_3C_2H_2O_2^-$	$Cu(CH_3COO)_2$
	440.820 (-39.1)	$Cu_3OC_8H_{12}O_8^-$	$Cu(CH_3COO)_2$
	444.727 (21.2)	$Cu_4O_4C_5H_5O_4^-$	$Cu(CH_3COO)_2$
	464.650 (-31.7)	$Cu_5O_2C_4H_6O_4^-$	$Cu(CH_3COO)_2$

10 July 2024 19:07:58



Accession #:

01953-01

<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> Verdigris, synthetic—Kremer Pigmente Ref. 44450 SIMS IONTOF, TOF SIMS IV Time of flight 2300 m/Δm 25 Da O₂⁻, Cl⁻, Cu⁻, CuO⁻, Cu₂O₂⁻, and Cu₃O₃⁻ 0° 45° LMIG Bi₃⁺ 1.0 × 10¹³ ion/cm² 0.8–1.2 ns 6.7 kHz 25 000 eV 0.000 31 nA 13.2 nA ~2 μm 100 × 100 μm² 45° Negative 0 Da 1995 Da Yes 617 s </p>
---	---

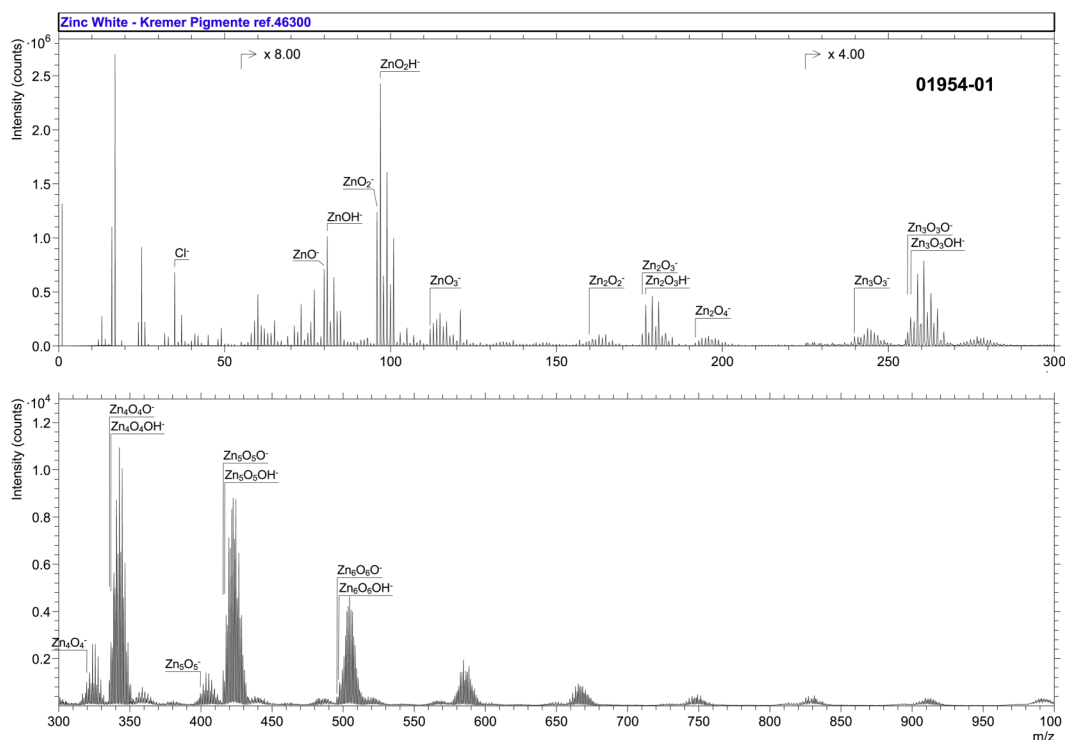
Surface was not flat, which impacted the mass resolution.
Peak at m/z 59.02 attributed to acetate ion $C_2H_3O_2^-$ was saturated.

10 July 2024 19:07:58

SPECTRAL FEATURES TABLE

Spectrum ID #	Mass (Δm), Da	Species	Peak Assignment
01954-01	79.925 (0.58)	ZnO ⁻	ZnO
	80.932 (-6.02)	ZnOH ⁻	—
	95.920 (0.39)	ZnO ₂ ⁻	ZnO
	96.927 (-5.50)	ZnO ₂ H ⁻	—
	111.914 (-0.95)	ZnO ₃ ⁻	ZnO
	159.849 (-1.06)	(ZnO) ₂ ⁻	ZnO
	175.842 (-8.44)	Zn ₂ O ₃ ⁻	ZnO
	176.851 (-3.88)	Zn ₂ O ₃ H ⁻	—
	191.839 (3.26)	Zn ₂ O ₄ ⁻	ZnO
	239.775 (8.80)	(ZnO) ₃ ⁻	ZnO
	255.766 (-6.07)	Zn ₃ O ₄ ⁻	ZnO
	256.775 (-1.65)	Zn ₃ O ₄ H ⁻	—
	319.701 (13.1)	(ZnO) ₄ ⁻	ZnO
	335.693 (4.34)	Zn ₄ O ₅ ⁻	ZnO
	336.704 (12.6)	Zn ₄ O ₅ H ⁻	—
	399.625 (10.2)	(ZnO) ₅ ⁻	ZnO
	415.611 (-11.0)	Zn ₅ O ₆ ⁻	ZnO
	416.620 (-9.50)	Zn ₅ O ₆ H ⁻	—
	495.532 (-16.3)	Zn ₆ O ₇ ⁻	ZnO
	496.543 (-10.2)	Zn ₆ O ₇ H ⁻	—

10 July 2024 19:07:58



Accession #:

01954-01

■ Specimen:

Zinc White—Kremer Pigmente Ref. 46300

■ Technique:

SIMS

Instrument:

IONTOF, TOF SIMS IV

Analyzer Type:

Time of flight

Analyzer Mass Resolving Power:

4500 m/Δm

Mass Resolving Power Determined at:

25 Da

Species Used for Mass Calibration:

Cl^- , ZnO_2^- , Zn_2O_3^- , Zn_3O_4^- , $^{66}\text{Zn}^{68}\text{ZnZn}_2\text{O}_6^-$, $^{66}\text{Zn}^{68}\text{Zn}_2\text{Zn}_4\text{O}_8^-$, and $^{66}\text{Zn}^{68}\text{Zn}_2\text{Zn}_5\text{O}_{10}^-$

Specimen Normal-to-Analyzer:

0°

Source-to-Analyzer Angle:

45°

Primary Beam Ion Gun:

LMIG

Primary Ion Species:

Bi_3^+

Primary Ion Dose:

4.37×10^{11} 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:

Negative

Mass Range Minimum:

0 Da

Mass Range Maximum:

3545 Da

Spectrum Dead Time Corrected:

Yes

Total Spectral Acquisition Time:

309 s

Comment:

Distinctive isotopic pattern for Zn. Peaks attributed to $\text{O}(\text{ZnO})_x^-$ are commonly present up to $x = 10$, with lower intensity.

10 July 2024 19:07:58