

ToF-SIMS spectra of historical inorganic pigments: Lead-based pigments in positive 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: Lead-based pigments in positive polarity. Surface Science Spectra, 2024, 31 (1), pp.015003. 10.1116/6.0003507. hal-04572572

HAL Id: hal-04572572

https://hal.science/hal-04572572

Submitted on 11 May 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.



RESEARCH ARTICLE | MAY 03 2024

ToF-SIMS spectra of historical inorganic pigments: Lead-based pigments in positive polarity © ©

Special Collection: ToF-SIMS Spectra of Historical Inorganic Pigments

Caroline Bouvier [0]; Sebastiaan Van Nuffel [0]; Alain Brunelle [22]



Surf. Sci. Spectra 31, 015003 (2024) https://doi.org/10.1116/6.0003507











ToF-SIMS spectra of historical inorganic pigments: Lead-based pigments in positive polarity (1)

Cite as: Surf. Sci. Spectra 31, 015003 (2024); doi: 10.1116/6.0003507

Submitted: 31 January 2024 · Accepted: 2 April 2024 ·

Published Online: 3 May 2024













AFFILIATIONS

- ¹Sorbonne Université, CNRS, Laboratoire d'Archéologie Moléculaire et Structurale, (LAMS), Paris, France
- ²Maastricht MultiModal Molecular Imaging Institute (M4i), Maastricht University, Maastricht, The Netherlands
- ³Faculty of Science and Engineering, Maastricht University, Maastricht, 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

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 database focuses on eight lead-based historical inorganic pigments, manufactured following traditional recipes. Lead pigments have been widely used in painting until the late 19th century. Here, the positive polarity ToF-SIMS reference spectra using a Bi₃ primary ion species are presented.

© 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/10.1116/6.0003507

Accession#: 01906, 01907, 01908, 01909, 01910, 01911, 01912, and 01913

Technique: SIMS

Specimen: Lead tin yellow I, Naples yellow, Lead white, Flake white

10μ, Flake white, Cerussite, Minium, and Litharge

Instrument: IONTOF, TOF SIMS IV

Major Species in Spectra: O, H, Si, S, Al, C, Na, Pb, K, Sb, and Sn

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. Here, we provide a ToF-SIMS spectral database for eight lead-based inorganic pigments. Lead-based pigments have been commonly used in all painting techniques until the late 19th century and, therefore, are very likely to be found when analyzing a historical painting sample. In particular, the pigment generally referred to as "lead white" can have various compositions depending on the manufacturing process, and this paper compares a selection of them (namely #01908, #01909, #01910, and #01911). For each, a list of their fragmentation products is given.

The reference materials were supplied by specialized manufacturers selling pigments reproducing historical recipes as closely as possible, such as Kremer Pigmente GmbH, Masters Pigments, Laverdure, and Sennelier. Pigments were available as finely ground powder of variable particle size (between one and a few tens of μ m) conditioned in glass-sealed vials. In paintings, pigment particles are not solubilized, 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 conductive

double-sided tape (3 M Electrically Conductive Adhesive Transfer Tape 9703) already fixed to a $1 \, \mathrm{cm} \times 1 \, \mathrm{cm} \times 0.125 \, \mathrm{mm}$ 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 ultrahigh vacuum (10^{-8} to 10^{-9} hPa) while ensuring a flat surface.

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. The primary ion dose $(25 \, \text{keV} \, \text{Bi}_3^+)$ was $4.35 \times 10^{11} \, \text{ions/cm}^2$. Surface potential was compensated.

All data were calibrated using the same set of peaks appearing in all spectra, namely, Na⁺ at m/z 22.99, Pb⁺ at m/z 207.98, Pb₂⁺ at m/z 415.95, Pb₂O⁺ at m/z 431.91, ²⁰⁶PbPb₂O₂⁺ at m/z 653.92, $^{206}\text{PbPb}_3\text{O}_3^+$ at m/z 877.89, and $^{206}\text{PbPb}_4\text{O}_4^+$ at m/z 1101.86. This calibration list allowed for a complete coverage of the mass range of interest, and the lead-containing calibration ions could easily be verified using their isotopic pattern. 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 (Ref. 1). In this context, the choice of 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 current literature (Refs. 2–6). The spectrum ID# refers to that number.

SPECIMEN DESCRIPTION (ACCESSION # 01906)

Specimen: Lead Tin Yellow I (Kremer Pigmente Ref. 10100)

CAS Registry #: 12143-43-0

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

linity; dielectric; inorganic compound; powder Chemical Name: Lead stannate Source: Kremer Pigmente GmbH

Specimen Composition: Pb₂SnO₄ **Form:** Ground pigment powder

History and Significance: A light-yellow pigment that was widely used in oil painting from the Middle Ages to the dawn of the 19th century. Prohibited today because of its lead content.

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 the stainless-steel 1×1 cm² 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: None

SPECIMEN DESCRIPTION (ACCESSION # 01907)

Specimen: Naples Yellow (Kremer Pigmente Ref. 43130)

CAS Registry #: 13510-89-9

Specimen Characteristics: Homogeneous; solid; unknown crystal-

linity; dielectric; inorganic compound; powder

Chemical Name: Lead antimonate **Source:** Kremer Pigmente GmbH

Specimen Composition: $Pb_2Sb_2O_7$ [and $Pb_3(SbO_4)_2$]

Form: Ground pigment powder

History and Significance: A yellow pigment used on Renaissance palettes, which is synthesized by heating a lead compound (oxide or nitrate) with an antimony compound (oxide, sulfide, or potassium antimonate). Particle size is in the micrometer range.

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 the stainless-steel 1×1 cm² 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: None

SPECIMEN DESCRIPTION (ACCESSION # 01908, 01909, 01910, 01911)

Specimen: (Accession #01908) Lead white (Kremer Pigmente Ref. 46000), (Accession #01909) Flake white $10\,\mu\text{m}$ (Masters Pigments Ref. 901010), (Accession #01910) Flake white (Sennelier PW No. 108), and (Accession #01911) Cerussite (Masters Pigments Ref. 951010)

CAS Registry #: (Accession #01908, 01911) 598-63-0 and (Accession #01909, 01910) 1319-46-6

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

Chemical Name: (Accession #01908, 01911) Lead (II) carbonate, synth. and (Accession #01909, 01910) Lead (II) carbonate, basic

Source: (Accession #01908) Kremer Pigmente GmbH, (Accession #01909, 01911) Masters Pigments, USA, and (Accession #01910) Sennelier, France

Specimen Composition: (Accession #01908, 01911) PbCO₃ and (Accession #01909, 01910) 2PbCO₃·Pb(OH)₂

Form: Ground pigment powder

History and Significance: The most widely used white pigment, progressively replaced during the beginning of the 20th century with newly available less toxic alternatives. A mixture of cerussite (lead carbonate) and hydrocerussite (basic lead carbonate) with proportions varying according to the manufacturing process, which can inform about the origin of the pigment. It is synthesized using lead strips, vinegar, CO₂, and heat. The latter two are usually provided by a fermenting material. In the presence of acetic acid vapors, the lead surface corrodes to lead acetate, which is then converted to basic lead carbonate in the presence of CO₂. This stable process has been used over centuries, its origins dating back to Ancient Greece and China. It was used as a cosmetic since ancient times.

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 the stainless-steel 1×1 cm² 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: None

SPECIMEN DESCRIPTION (ACCESSION # 01912)

Specimen: Minium/Red Lead (Kremer Pigmente Ref. 42500) CAS Registry #: 1314-41-6

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

Chemical Name: Lead tetraoxide Source: Kremer Pigmente GmbH Specimen Composition: Pb₃O₄ Form: Ground pigment powder

History and Significance: This naturally occurring lead oxide has been synthesized since early times by heating lead carbonates. Its color approaches that of cinnabar, providing a cheaper alternative. Used since ancient Greek times as a rust inhibitor for metals, it remained its main use in the 20th century until it was banned in the 1990s.

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 the stainless-steel 1×1 cm² 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: None

SPECIMEN DESCRIPTION (ACCESSION # 01913)

Specimen: Massicot, Litharge (Kremer Pigmente Ref. 43010)

CAS Registry #: 1317-36-8

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

Chemical Name: Lead (II) oxide Source: Kremer Pigmente GmbH Specimen Composition: PbO Form: Ground pigment powder

History and Significance: Litharge and massicot are lead monoxide polymorphs with the formula PbO, respectively, red and yellow-orange in appearance. They are both formed by heating lead or lead white. Litharge plays a key role in the preparation of drying oil for painting: when mixed, it accelerates the polymerization of the film.

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 the stainless-steel 1×1 cm² 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: None

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 (Θe): 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 µm

Beam Raster Size: $250 \times 250 \,\mu\text{m}^2$ 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 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 µm

Beam Raster Size: $500 \times 500 \,\mu\text{m}^2$ 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 the 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

A.B. conceived and designed the analysis. S.V.N. and C.B. collected data. C.B. performed the analysis. All authors contributed to the writing of the manuscript the writing of the manuscript.

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

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 (Archetype, London, 1986), Vol. 1.

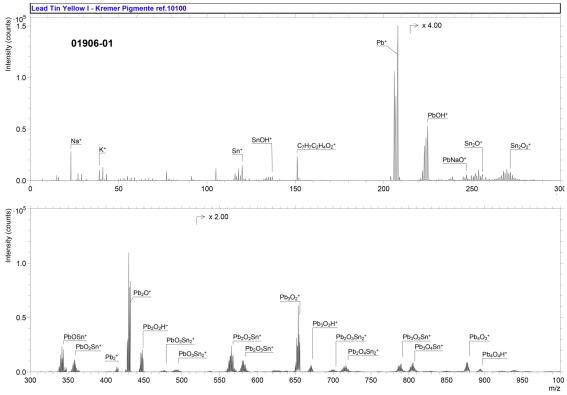
⁴A. Roy, Artists' Pigments: A Handbook of Their History and Characteristics (Archetype, London, 1993), Vol. 2.

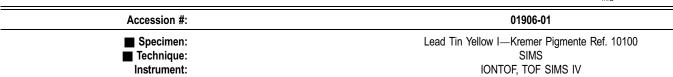
⁵E. W. FitzHugh, Artists' Pigments: A Handbook of Their History and Characteristics (Archetype, London, 1997), Vol. 3.

⁶J. R. Barnett, S. Miller, and E. Pearce, Opt. Laser Technol. 38, 445 (2006).

SPECTRAL FEATURES TABLE

	Lead Tin Yellow I—Kremer Pigmente Ref. 10100—Positive polarity		
Spectrum ID #	Mass (∆m), Da	Species	Peak Assignmen
01906-01	38.964 (19.1)	K ⁺	Impurity
	119.898 (-27.2)	Sn ⁺	Pb ₂ SnO ₄
	136.906 (8.38)	SnOH ⁺	Pb ₂ SnO ₄
	246.967 (25.9)	PbNaO ⁺	Impurity
	255.796 (-12.3)	Sn ₂ O+	Pb ₂ SnO ₄
	271.802 (-30.2)	Sn ₂ O ₂ +	Pb ₂ SnO ₄
	343.873 (0.13)	PbOSn ⁺	Pb ₂ SnO ₄
	359.877 (23.5)	PbO ₂ Sn ⁺	Pb ₂ SnO ₄
	479.793 (46.3)	PbO ₂ Sn ₂ ⁺	Pb ₂ SnO ₄
	495.774 (17.1)	PbO ₃ Sn ₂ +	Pb ₂ SnO ₄
	567.825 (-34.5)	Pb ₂ O ₂ Sn ⁺	Pb ₂ SnO ₄
	583.835 (-8.35)	Pb ₂ O₃Sn⁺	Pb ₂ SnO ₄
	703.743 (2.21)	$Pb_2O_3Sn_2^+$	Pb ₂ SnO ₄
	719.750 (17.8)	$Pb_2O_4Sn_2^{+}$	Pb ₂ SnO ₄
	791.814 (-3.15)	$Pb_3^{-}O_3^{-}Sn^{+}$	Pb ₂ SnO ₄
	807.823 (14.2)	$Pb_3O_4Sn^+$	Pb ₂ SnO ₄
	1015.791 (2.59)	Pb ₄ O ₄ Sn ⁺	Pb ₂ SnO ₄
	1031.782 (-0.63)	Pb₄O₅Sn ⁺	Pb ₂ SnO ₄

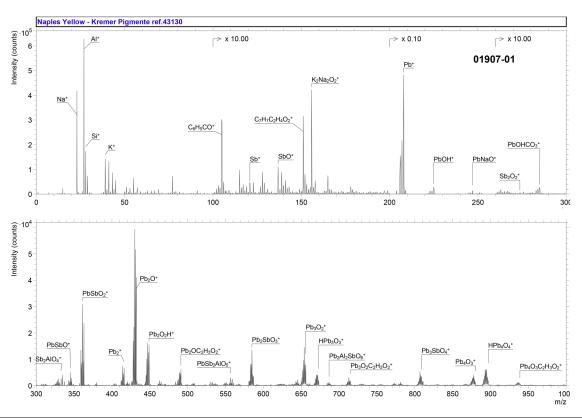






Accession #:	01906-01	
Analyzer Type:	Time-of-flight	
Analyzer Mass Resolution:	3100 m/∆m	
Mass Resolution Determined at:	27 Da	
Species Used for Mass Calibration:	Na ⁺ , Pb ⁺ , Pb ₂ ⁺ , Pb ₂ O ⁺ , ²⁰⁶ PbPb ₂ O ₂ ⁺ , ²⁰⁶ PbPb ₃ O ₃ ⁺ , and ²⁰⁶ PbPb ₄ O ₄ ⁺	
Specimen Normal-to-Analyzer:	0°	
Source-to-Analyzer Angle:	45°	
Primary Beam Ion Gun:	LMIG	
Primary Ion Species:	Bi ₃ ⁺	
Primary Ion Dose:	$4.34 \times 10^{11} \text{ ion/cm}^2$	
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 21 nA	
DC Beam Current:	14.4 nA	
Beam Diameter:	\sim 2 μ m	
Beam Raster Size:	$250 \times 250 \mu\text{m}^2$	
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:	207 s	
Comment:	Distinctive isotopic pattern	

	Naples Yellow—Kremer Pigmente Ref. 43130—Positive polarity		
Spectrum ID #	Mass (∆m), Da	Species	Peak Assignment
01907-01	26.982 (23.4)	Al^+	Impurity, likely from the manufacturing process
	27.976 (-32.2)	Si ⁺	Impurity, likely from the manufacturing process
	38.965 (36.8)	K ⁺	Impurity, likely from the manufacturing process
	120.900 (-25.5)	Sb ⁺	$Pb_2Sb_2O_7/Pb_3(SbO_4)_2$
	136.901 (22.6)	SbO ⁺	$Pb_2Sb_2O_7/Pb_3(SbO_4)_2$
	155.895 (-11.0)	$K_2Na_2O_2^+$	Impurity, likely from the manufacturing process
	272.802 (18.5)	$Sb_2O_2^+$	$Pb_2Sb_2O_7/Pb_3(SbO_4)_2$
	332.779 (33.2)	Sb ₂ AlO ₄ ⁺	
	344.883 (24.1)	PbSbO [÷]	$Pb_2Sb_2O_7/Pb_3(SbO_4)_2$
	360.881 (31.4)	PbSbO ₂ ⁺	$Pb_2Sb_2O_7/Pb_3(SbO_4)_2$
	490.954 (-14.8)	$Pb_2OC_2H_3^-O_2^+$	
	556.740 (-0.48)	PbSb ₂ AlO ₅ ⁺	_
	584.855 (23.9)	Pb ₂ SbO ₃ ⁺	$Pb_2Sb_2O_7/Pb_3(SbO_4)_2$
	686.808 (27.4)	$Pb_2SbAl_2O_6^+$	
	714.920 (-18.0)	Pb ₃ O ₂ C ₂ H ₃ O ₂ ⁺	_
	808.828 (18.2)	Pb ₃ SbO ₄ ⁺	$Pb_2Sb_2O_7/Pb_3(SbO_4)_2$
	938.892 (-12.6)	$Pb_4O_3C_2H_3O_2^+$	_
	1120.893 (24.6)	$Pb_5O_5H^{\dagger}$	$Pb_2Sb_2O_7/Pb_3(SbO_4)_2$



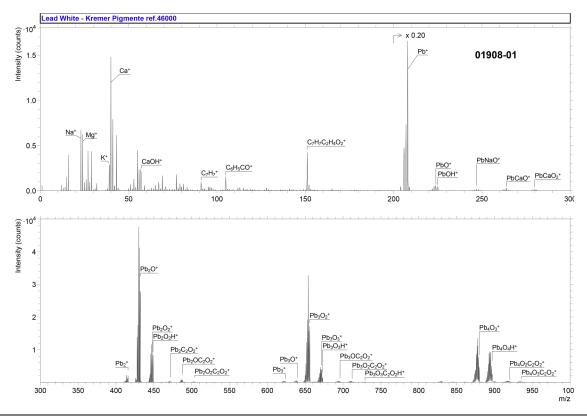
01907-01 Accession #: ■ Specimen: Naples Yellow-Kremer Pigmente Ref. 43130 Technique: SIMS IONTOF, TOF SIMS IV Instrument:



Accession #:	01907-01
Analyzer Type:	Time-of-flight
Analyzer Mass Resolution:	2600 m/∆m
Mass Resolution Determined at:	27 Da
Species Used for Mass Calibration:	Na^+ , Pb^+ , Pb_2^+ , Pb_2O^+ , $^{206}PbPb_2O_2^+$, $^{206}PbPb_3O_3^+$, and $^{206}PbPb_4O_4^+$
Specimen Normal-to-Analyzer:	0°
Source-to-Analyzer Angle:	45°
Primary Beam Ion Gun:	LMIG
Primary Ion Species:	Bi_3^+
Primary Ion Dose:	4.34×10^{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 21 nA
DC Beam Current:	14.6 nA
Beam Diameter:	\sim 2 μ m
Beam Raster Size:	$250 \times 250 \mu\text{m}^2$
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:	210 s
Comment:	Distinctive isotopic pattern, allowing to discriminate between SnOH ⁺ (theoretical mass 136.904) and SbO ⁺
	(theoretical mass 136.898)



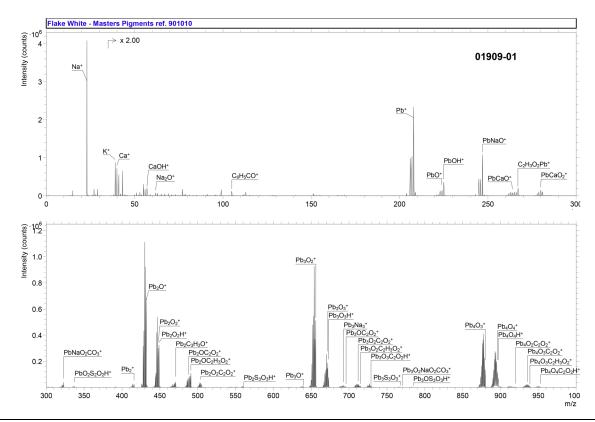
Lead White—Kremer Pigmente Ref. 46000—Positive polarity			
Spectrum ID #	Mass (∆m), Da	Species	Peak Assignment
01908-01	23.984 (-3.22)	$Mg^{\scriptscriptstyle{+}}$	_
	38.965 (38.5)	K [∓]	_
	39.962 (-9.51)	Ca [⁺]	_
	56.966 (17.5)	CaOH ⁺	_
	91.057 (25.0)	$C_7H_7^+$	_
	105.035 (15.2)	C ₆ H ₅ CO ⁺	Phthalate contamination
	151.080 (28.3)	$C_7H_7(CH_2O)_2^+$	_
	223.972 (4.36)	PbO ⁺	PbCO ₃
	246.964 (12.5)	PbNaO ⁺	
	263.940 (23.6)	PbCaO ⁺	_
	279.931 (7.79)	PbCaO ₂ ⁺	_
	447.960 (38.0)	$Pb_2O_2^+$	PbCO ₃
	471.961 (39.1)	$Pb_2(CO)_2^+$	PbCO ₃
	487.933 (-10.2)	$Pb_2O(CO)_2^+$	PbCO ₃
	503.914 (-36.4)	$Pb_2O_2(CO)_2^+$	PbCO ₃
	623.933 (5.53)	Pb ₃ ⁺	PbCO ₃
	639.909 (-23.6)	Pb ₃ O ⁺	PbCO ₃
	671.914 (-0.23)	$Pb_3O_3^+$	PbCO ₃
	695.898 (-23.7)	$Pb_3O(CO)_2^+$	PbCO ₃
	711.894 (-21.4)	$Pb_3O_2(CO)_2^+$	PbCO ₃
	728.902 (-13.2)	$Pb_3O_3C_2O_2H^+$	PbCO ₃
	919.865 (-22.1)	$Pb_4O_2(CO)_2^+$	PbCO ₃
	935.869 (-11.9)	$Pb_4O_3(CO)_2^{+}$	PbCO ₃
	1039.876 (-6.42)	Pb ₅ ⁺	PbCO ₃
	1120.856 (-8.22)	$Pb_5O_5^{\circ}H^{+}$	DI 00
	1327.827 (-4.87)	$Pb_6O_5^+$	PbCO ₃ PbCO ₃ PbCO ₃
	1344.832 (-3.10)	$Pb_6O_6H^+$	PbCO ₃



11 May 2024 11:58:33 01908-01 Accession #: ■ Specimen: Lead White—Kremer Pigmente Ref. 46000 ■ Technique: SIMS IONTOF, TOF SIMS IV Instrument: Analyzer Type: Time-of-flight **Analyzer Mass Resolution:** 4000 m/∆m Mass Resolution Determined at: 27 Da $Na^+, Pb^+, Pb_2^+, Pb_2O^+, ^{206}PbPb_2O_2^+, ^{206}PbPb_3O_3^+, and ^{206}PbPb_4O_4^+$ Species Used for Mass Calibration: Specimen Normal-to-Analyzer: 0° Source-to-Analyzer Angle: 45° Primary Beam Ion Gun: **LMIG** Bi_3^+ 4.37 × 10¹¹ ion/cm² **Primary Ion Species:** Primary Ion Dose: Primary Ion Pulse Width: $0.8 - 1.2 \, \text{ns}$ Primary Ion Pulse Rate: 5 kHz 25 000 eV Net Beam Voltage: **Pulsed Beam Current:** 0.000 16 nA DC Beam Current: 15.7 nA Beam Diameter: \sim 2 μ m Beam Raster Size: $250 \times 250 \,\mu\text{m}^2$ 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:** 250 s Comment: Assignments were refined using isotopic patterns.

≤
Mav
N
024
_
.58

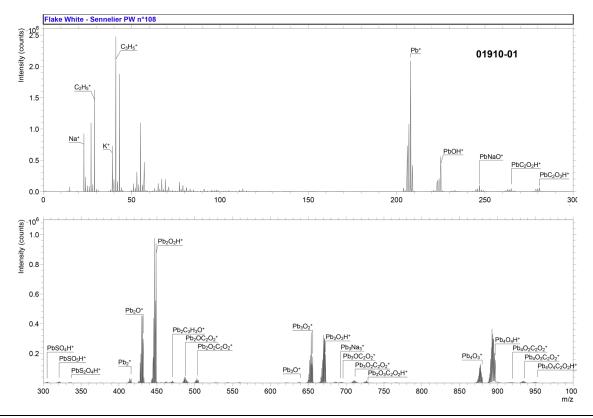
Flake White 10μ—Masters Pigments Ref. 901010—Positive polarity			
Spectrum ID #	Mass (∆m), Da	Species	Peak Assignment
01909-01	38.963 (2.82)	K⁺	_
	39.960 (-58.9)	Ca⁺	_
	56.963 (-26.3)	CaOH⁺	_
	61.975 (22.7)	Na ₂ O⁺	_
	105.037 (31.7)	C ₆ H ₅ CO ⁺	Phthalate contamination
	223.976 (22.9)	PbO ⁺	2PbCO ₃ .Pb(OH) ₂
	246.974 (54.7)	PbNaO⁺	
	263.947 (48.9)	PbCaO⁺	_
	267.006 (62.5)	$C_2H_3O_2Pb^+$	From lead acetate
	279.938 (34.2)	PbCaO ₂ ⁺	_
	322.951 (33.3)	PbNaO ₂ CO ₃ ⁺	_
	336.895 (-38.7)	$PbS_2O_4H^+$	_
	447.950 (16.3)	$Pb_2O_2^+$	2PbCO ₃ ·Pb(OH) ₂
	470.942 (-61.1)	$Pb_2C_3H_3O^{\dagger}$	2PbCO ₃ ·Pb(OH) ₂
	471.941 (-3.48)	$Pb_2(CO)_2^+$	2PbCO ₃ ·Pb(OH) ₂
	487.934 (-7.58)	$Pb_2O(CO)_2^+$	2PbCO ₃ ·Pb(OH) ₂
	490.965 (8.80)	$Pb_2OC_2H_3O_2^+$	From lead acetate
	503.903 (-59.1)	$Pb_2O_2(CO)_2^+$	2PbCO ₃ ·Pb(OH) ₂
	560.835 (-47.3)	$Pb_2S_3O_3H^+$	_
	623.922 (-12.5)	Pb ₃ ⁺	2PbCO ₃ ·Pb(OH) ₂
	639.920 (-6.39)	Pb₃O ⁺	2PbCO ₃ ·Pb(OH) ₂
	671.920 (9.20)	$Pb_3O_3^+$	2PbCO ₃ ·Pb(OH) ₂
	692.906 (10.2)	Pb ₃ Na ₃ ⁺	_ , , ,
	694.914 (-41.9)	$Pb_3OC_3H_3O^+$	2PbCO ₃ ·Pb(OH) ₂
	695.907 (-10.4)	$Pb_3O(CO)_2^+$	2PbCO ₃ ·Pb(OH) ₂
	711.901 (-11.3)	$Pb_3O_2(CO)_2^+$	2PbCO ₃ ·Pb(OH) ₂
	714.938 (7.74)	$Pb_3O_2C_2H_3O_2^+$	From lead acetate
	728.876 (-48.8)	$Pb_3O_3(CO)_2H^+$	2PbCO ₃ ·Pb(OH) ₂
	767.842 (14.8)	$Pb_3S_3O_3^+$	_
	770.874 (-12.3)	Pb ₃ O ₂ NaO ₂ CO ₃ ⁺	-
	784.822 (-13.7)	$Pb_3OS_3O_3H^{\dagger}$	_
	895.896 (11.4)	$Pb_4O_4^+$	2PbCO ₃ ·Pb(OH) ₂
	919.879 (-6.78)	$Pb_4O_2(CO)_2^+$	2PbCO ₃ ·Pb(OH) ₂
	935.893 (13.5)	$Pb_4O_3(CO)_2^+$	2PbCO ₃ ·Pb(OH) ₂
	938.923 (19.8)	$Pb_4O_3C_2H_3O_2^+$	From lead acetate
	952.844 (-41.6)	$Pb_4O_4(CO)_2H^+$	2PbCO ₃ ·Pb(OH) ₂
	1119.877 (17.9)	Pb ₅ O ₅ ⁺	2PbCO ₃ ·Pb(OH) ₂
	1120.876 (10.1)	$Pb_{5}O_{5}H^{+}$	2PbCO ₃ ·Pb(OH) ₂
	1327.849 (11.5)	Pb ₆ O ₅ ⁺	2PbCO ₃ ·Pb(OH) ₂
	1343.857 (20.7)	$Pb_6O_6^+$	2PbCO ₃ ·Pb(OH) ₂
	1344.862 (19.4)	$Pb_6O_6H^{+}$	2PbCO ₃ ·Pb(OH) ₂



11 May 2024 11:58:33 01909-01 Accession #: ■ Specimen: Flake White 10µ—Masters Pigments Ref. 901010 ■ Technique: SIMS IONTOF, TOF SIMS IV Instrument: Analyzer Type: Time-of-flight **Analyzer Mass Resolution:** 4400 m/∆m Mass Resolution Determined at: 27 Da ${\rm Na^+,\,Pb^+,\,Pb_2^+,\,Pb_2O^+,\,^{206}PbPb_2O_2^+,\,^{206}PbPb_3O_3^+,\,and\,^{206}PbPb_4O_4^+}$ Species Used for Mass Calibration: Specimen Normal-to-Analyzer: 0° 45° Source-to-Analyzer Angle: **LMIG** Primary Beam Ion Gun: Bi_3^+ 4.37 × 10¹¹ ion/cm² **Primary Ion Species:** Primary Ion Dose: $0.8 - 1.2 \, \text{ns}$ Primary Ion Pulse Width: Primary Ion Pulse Rate: 8.3 kHz Net Beam Voltage: 25 000 eV Pulsed Beam Current: 0.000 38 nA DC Beam Current: 1.9 nA Beam Diameter: $\sim 2 \mu \text{m}$ Beam Raster Size: $200 \times 200 \,\mu\text{m}^2$ Beam Incident Angle: 45° Positive Secondary Source Polarity: Mass Range Minimum: 0 Da 1995 Da Mass Range Maximum: Spectrum Dead Time Corrected: Yes **Total Spectral Acquisition Time:** 161 s Comment: Assignments were refined using isotopic patterns.



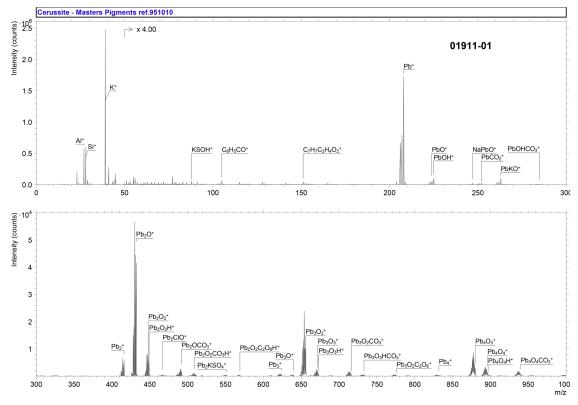
Flake White—Sennelier PW No. 108— Positive polarity			
Spectrum ID #	Mass (∆m), Da	Species	Peak Assignment
1910-01	38.965 (37.1)	K ⁺	_
	246.974 (54.8)	PbNaO ⁺	_
	264.979 (20.1)	$PbC_2O_2H^+$	2PbCO ₃ ·Pb(OH) ₂
	280.952 (-58.2)	$PbC_2O_3H^+$	2PbCO ₃ ·Pb(OH) ₂
	304.949 (43.6)	PbSO₄H ⁺	_
	320.928 (-8.09)	PbSO ₅ H ⁺	_
	336.898 (-28.9)	$PbS_2O_4H^+$	_
	470.941 (—63.6)	$Pb_2C_3H_3O^+$	2PbCO ₃ .Pb(OH) ₂
	471.927 (—32.2)	$Pb_2(CO)_2^+$	_
	487.926 (—22.8)	$Pb_2O(CO)_2^+$	2PbCO ₃ ·Pb(OH) ₂
	503.910 (-44.4)	$Pb_2O_2(CO)_2^+$	2PbCO ₃ ·Pb(OH) ₂
	528.927 (36.7)	Pb ₂ O ₂ SO ₃ H ⁺	
	544.890 (-22.6)	Pb ₂ O ₃ SO ₃ H ⁺	_
	560.841 (-36.8)	$P_{b_2}^{\overline{b_2}}S_3O_3H^{\dagger}$	_
	639.917 (-12.0)	Pb ₃ O ⁺	2PbCO ₃ ·Pb(OH) ₂
	692.893 (-8.49)	Pb ₃ Na ₃ ⁺	
	694.901 (—59.7)	$Pb_3OC_3H_3O^+$	2PbCO ₃ ·Pb(OH) ₂
	695.889 (-35.8)	$Pb_3O(CO)_2^+$	2PbCO ₃ ·Pb(OH) ₂
	711.894 (—21.1)	$Pb_3O_2(CO)_2^{+}$	2PbCO ₃ ·Pb(OH) ₂
	728.886 (-35.4)	Pb ₃ O ₃ (CO) ₂ H ⁺	2PbCO ₃ ·Pb(OH) ₂
	752.878 (_ 1.19)	Pb ₃ O ₃ SO ₃ H ⁺	_
	767.842 (15.6)	$Pb_3S_3O_3^+$	_
	784.827 (_7.91)	$Pb_3OS_3O_3H^{\dagger}$	_
	919.868 (-19.8)	$Pb_4O_2(CO)_2^+$	2PbCO ₃ ·Pb(OH) ₂
	935.859 (-23.2)	$Pb_4O_3(CO)_2^+$	2PbCO ₃ ·Pb(OH) ₂
	952.846 (-39.0)	$Pb_4O_4(CO)_2H^+$	2PbCO ₃ ·Pb(OH) ₂
	1120.873 (7.40)	Pb ₅ O ₅ H ⁺	2PbCO ₃ ·Pb(OH) ₂
	1327.834 (-0.10)	$Pb_6O_5^+$	2PbCO ₃ ·Pb(OH) ₂
	1344.856 (14.8)	Pb ₆ O ₆ H ⁺	2PbCO ₃ ·Pb(OH) ₂



	m/z	
Accession #:	## D1910-01 Flake White—Sennelier PW No. 108 11.58 10.000	
■ Specimen:	Flake White—Sennelier PW No. 108	
■ Technique:	SIMS 58	
Instrument:	IONTOF, TOF SIMS IV	
Analyzer Type:	Time-of-flight	
Analyzer Mass Resolution:	3500 m/∆m	
Mass Resolution Determined at:	27 Da	
Species Used for Mass Calibration:	Na^+ , Pb^+ , Pb_2^+ , Pb_2O^+ , $^{206}PbPb_2O_2^+$, $^{206}PbPb_3O_3^+$, and $^{206}PbPb_4O_4^+$	
Specimen Normal-to-Analyzer:	0°	
Source-to-Analyzer Angle:	45°	
Primary Beam Ion Gun:	LMIG	
Primary Ion Species:	Bi ⁺ ₃	
Primary Ion Dose:	$4.37 \times 10^{11} \text{ ion/cm}^2$	
Primary Ion Pulse Width:	0.8–1.2 ns	
Primary Ion Pulse Rate:	8.3 kHz	
Net Beam Voltage:	25 000 eV	
Pulsed Beam Current:	0.00038 nA	
DC Beam Current:	1.9 nA	
Beam Diameter:	\sim 2 μ m	
Beam Raster Size:	$200 \times 200 \mu\text{m}^2$	
Beam Incident Angle:	45°	
Secondary Source Polarity:	Positive	
Mass Range Minimum:	0 Da	
Mass Range Maximum:	1995 Da	
Spectrum Dead Time Corrected:	Yes	
Total Spectral Acquisition Time:	161 s	
Comment:	None	



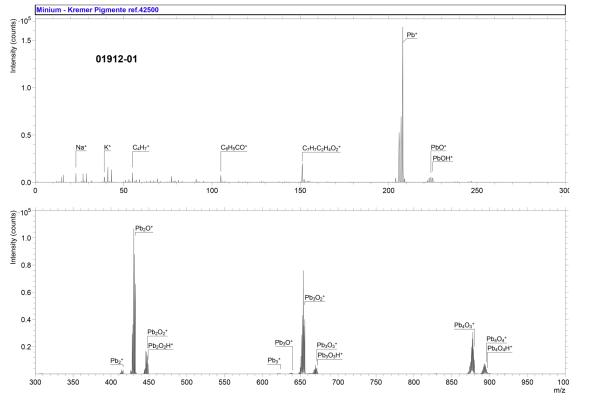
Cerussite—Masters Pigments Ref. 951010—Positive polarity			
Spectrum ID #	Mass (∆m), Da	Species	Peak Assignment
01911-01	26.981 (0.75)	Al ⁺	_
	27.975 (-40.3)	Si ⁺	_
	38.965 (57.4)	K ⁺	_
	87.939 (13.3)	KSOH⁺	_
	105.037 (37.2)	C ₆ H ₅ CO ⁺	Phthalate contamination
	151.080 (31.4)	$C_7H_7(CH_2O)_2^+$	_
	223.978 (30.4)	PbO ⁺	PbCO ₃
	246.968 (28.2)	PbONa ⁺	
	251.958 (-33.2)	PbCO ₂ ⁺	PbCO ₃
	262.944 (35.3)	PbOK ⁺	<u> </u>
	284.965 (6.59)	PbOHCO ₃ ⁺	PbCO ₃
	447.957 (31.9)	$Pb_2O_2^+$	PbCO ₃
	466.935 (39.8)	Pb ₂ CIO ⁺	<u> </u>
	491.950 (36.3)	Pb ₂ OCO ₃ ⁺	PbCO ₃
	508.951 (30.3)	$Pb_2O_2CO_3H^+$	PbCO ₃
	550.890 (38.9)	$Pb_2KSO_4^+$	
	568.903 (-28.9)	$Pb_2O_2C_2O_6H^+$	PbCO ₃
	623.933 (6.06)	Pb ₃	PbCO ₃
	639.914 (-16.8)	Pb₃O ⁺	PbCO ₃
	671.922 (11.9)	$Pb_3O_3^+$	PbCO ₃
	715.923 (26.3)	Pb ₃ O ₂ CO ₃ ⁺	PbCO ₃
	732.925 (25.2)	Pb ₃ O ₃ HCO ₃ ⁺	PbCO ₃
	775.922 (42.9)	$Pb_3O_2C_2O_6^{\dagger}$	PbCO ₃
	895.898 (13.6)	$Pb_4O_4^{\frac{1}{4}}$	PbCO ₃
	939.888 (13.8)	$Pb_4O_4CO_2^+$	PbCO ₃
	1327.847 (10.2)	Pb ₆ O ₅ ⁺	PbCO ₃



11 May 2024 11:58:33 Accession #: 01911-01 ■ Specimen: Cerussite—Masters Pigments Ref. 951010 SIMS ■ Technique: Instrument: IONTOF, TOF SIMS IV Analyzer Type: Time-of-flight **Analyzer Mass Resolution:** 2300 m/∆m Mass Resolution Determined at: 28 Da Na $^+$, Pb $^+$, Pb $_2^+$, Pb $_2$ O $^+$, 206 PbPb $_2$ O $_2^+$, 206 PbPb $_3$ O $_3^+$, and 206 PbPb $_4$ O $_4^+$ Species Used for Mass Calibration: Specimen Normal-to-Analyzer: 45° Source-to-Analyzer Angle: **LMIG** Primary Beam Ion Gun: Bi_3^+ 4.35 × 10¹¹ ion/cm² **Primary Ion Species:** Primary Ion Dose: Primary Ion Pulse Width: $0.8 - 1.2 \, \text{ns}$ Primary Ion Pulse Rate: 5 kHz Net Beam Voltage: 25 000 eV 0.000 23 nA **Pulsed Beam Current:** DC Beam Current: 7.2 nA Beam Diameter: \sim 2 μ m Beam Raster Size: $250 \times 250 \,\mu\text{m}^2$ 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:** 194 s Comment: None



Minium—Kremer Pigmente Ref. 42500—Positive polarity			
Spectrum ID #	Mass (∆m), Da	Species	Peak Assignment
01912-01	38.965 (51.4)	K ⁺	_
	55.058 (58.6)	$C_4H_7^+$	_
	91.058 (37.2)	C ₇ H ₇ ⁺	_
	105.037 (37.2)	C ₆ H ₅ CO ⁺	Phthalate contamination
	151.079 (26.4)	$C_7H_7(CH_2O)_2^+$	_
	223.973 (10.8)	PbO ⁺	Pb ₃ O ₄
	447.961 (40.5)	$Pb_2O_2^+$	Pb ₃ O ₄
	623.928 (-3.03)	Pb ₃ ⁺	Pb ₃ O ₄
	639.924 (-0.56)	Pb₃O ⁺	Pb ₃ O ₄
	671.921 (10.4)	Pb ₃ O ₃ ⁺	Pb ₃ O ₄
	895.901 (16.8)	$Pb_4O_4^{\frac{1}{4}}$	Pb ₃ O ₄
	1119.892 (31.1)	Pb ₅ O ₅ ⁺	Pb ₃ O ₄
	1120.903 (33.6)	$Pb_5O_5H^+$	Pb ₃ O ₄
	1327.837 (2.69)	$Pb_6O_5^+$	Pb ₃ O ₄



Accession #:	01912-01
■ Specimen:	Minium—Kremer Pigmente Ref. 42500
■ Technique:	SIMS
Instrument:	IONTOF, TOF SIMS IV
Analyzer Type:	Time-of-flight
Analyzer Mass Resolution:	3900 m/∆m

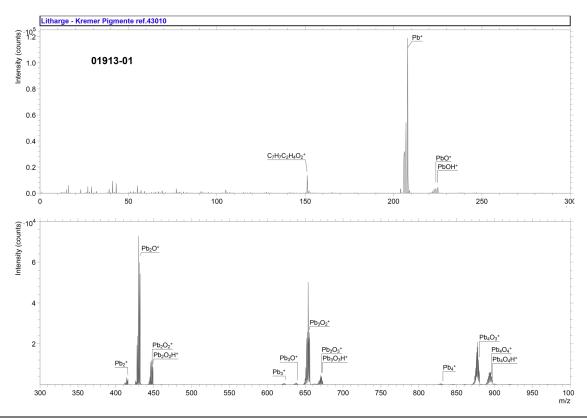
11 May 2024 11:58:33



Accession #:	01912-01	
Mass Resolution Determined at:	27 Da	
Species Used for Mass Calibration:	Na ⁺ , Pb ⁺ , Pb ₂ , Pb ₂ O ⁺ , ²⁰⁶ PbPb ₂ O ₂ ⁺ , ²⁰⁶ PbPb ₃ O ₃ ⁺ , and ²⁰⁶ PbPb 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 23 nA	
DC Beam Current:	7.2 nA	
Beam Diameter:	\sim 2 μ m	
Beam Raster Size:	$250 \times 250 \mu\text{m}^2$	
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:	194 s	
Comment:	None	



Litharge—Kremer Pigmente Ref. 43010—Positive polarity				
Spectrum ID #	Mass (∆m), Da	Species	Peak Assignment	
01913-01	151.083 (56.4)	C ₇ H ₇ (CH ₂ O) ₂ ⁺	_	
	223.973 (10.4)	PbO ⁺	PbO	
	447.957 (33.2)	$Pb_2O_2^+$	PbO	
	623.937 (12.8)	Pb ₃ ⁺	PbO	
	639.932 (11.8)	$Pb_3\overset{\circ}{O}^+$	PbO	
	671.939 (37.1)	$Pb_3^{\dagger}O_3^{\dagger}$	PbO	
	1039.868 (-14.5)	Pb_5^+	PbO	
	1120.876 (9.39)	$Pb_5O_5^{\circ}H^+$	PbO	



11 May 2024 11:58:33

Accession #:	01913-01	
■ Specimen:	Litharge—Kremer Pigmente Ref. 43010	
■ Technique:	SIMS	
Instrument:	IONTOF, TOF SIMS IV	
Analyzer Type:	Time-of-flight	
Analyzer Mass Resolution:	2100 m/∆m	
Mass Resolution Determined at:	27 Da	
Species Used for Mass Calibration:	Na^+ , Pb^+ , Pb_2^+ , Pb_2O^+ , $^{206}PbPb_2O_2^+$, $^{206}PbPb_3O_3^+$, and $^{206}PbPb_4O_4^+$	
Specimen Normal-to-Analyzer:	0°	
Source-to-Analyzer Angle:	45°	
Primary Beam Ion Gun:	LMIG	
Primary Ion Species:	Bi ₃ ⁺	



Accession #:	01913-01	
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 23 nA	
DC Beam Current:	7.2 nA	
Beam Diameter:	\sim 2 μ m	
Beam Raster Size:	$250 \times 250 \mu\text{m}^2$	
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:	194 s	
Comment:	None	

SPECTRAL FEATURES TABLE (peaks appearing in all spectra)					
Spectrum ID #	Mass (∆m), Da	Species	Peak Assignment		
All	22.99 (16.6)	Na ⁺	_		
•••	207.98 (9.1)	Pb ⁺	All lead-containing pigments		
•••	224.98 (18.1)	PbOH ⁺	All lead-containing pigments		
•••	415.95 (16.3)	Pb ₂ ⁺	All lead-containing pigments		
•••	431.96 (19.9)	Pb_2O^+	All lead-containing pigments		
•••	448.97 (36.2)	$Pb_2O_2H^+$	All lead-containing pigments		
•••	655.92 (4.2)	$Pb_3O_2^+$	All lead-containing pigments		
•••	672.93 (9.3)	$Pb_3O_3H^+$	All lead-containing pigments		
***	879.89 (8.1)	$Pb_4O_3^+$	All lead-containing pigments		
	896.89 (17.6)	$Pb_4O_4H^+$	All lead-containing pigments		
	1103.87 (3.1)	$Pb_5O_4^+$	All lead-containing pigments		

(Mean absolute deviation values are given for the mass deviations.)