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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  ; Sebastiaan Van Nuffel  ; Alain Brunelle  

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



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## AFFILIATIONS

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

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## 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 Bi<sup>+</sup> primary ion species are presented.

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

**Technique:** SIMS

**Specimen:** Lead tin yellow I, Naples yellow, Lead white, Flake white 10 $\mu$ , 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  $\mu$ 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 mm<sup>2</sup> piece of conductive

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double-sided tape (3 M Electrically Conductive Adhesive Transfer Tape 9703) already fixed to a 1 cm × 1 cm × 0.125 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 ( $10^{-8}$  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  $2 \times 10^{15}$  ions/cm<sup>2</sup>). Analyses were then performed on a  $250 \times 250 \mu\text{m}^2$  area centered in this larger cleaned area, rastered over  $128 \times 128$  pixels using the high current bunched mode. The primary ion dose (25 keV Bi<sub>3</sub><sup>+</sup>) was  $4.35 \times 10^{11}$  ions/cm<sup>2</sup>. Surface potential was compensated.

All data were calibrated using the same set of peaks appearing in all spectra, namely, Na<sup>+</sup> at  $m/z$  22.99, Pb<sup>+</sup> at  $m/z$  207.98, Pb<sub>2</sub><sup>+</sup> at  $m/z$  415.95, Pb<sub>2</sub>O<sup>+</sup> at  $m/z$  431.91, <sup>206</sup>PbPb<sub>2</sub>O<sub>2</sub><sup>+</sup> at  $m/z$  653.92, <sup>206</sup>PbPb<sub>3</sub>O<sub>3</sub><sup>+</sup> at  $m/z$  877.89, and <sup>206</sup>PbPb<sub>4</sub>O<sub>4</sub><sup>+</sup> 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 C<sub>2</sub>H<sub>3</sub><sup>+</sup>, C<sub>3</sub>H<sub>5</sub><sup>+</sup>, C<sub>4</sub>H<sub>7</sub><sup>+</sup>, and C<sub>7</sub>H<sub>7</sub><sup>+</sup>). 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

**Chemical Name:** Lead stannate

**Source:** Kremer Pigmente GmbH

**Specimen Composition:** Pb<sub>2</sub>SnO<sub>4</sub>

**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  $1 \times 1 \text{cm}^2$  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  $1 \times 10^{-5}$  and  $1 \times 10^{-6}$  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 crystallinity; dielectric; inorganic compound; powder

**Chemical Name:** Lead antimonate

**Source:** Kremer Pigmente GmbH

**Specimen Composition:** Pb<sub>2</sub>Sb<sub>2</sub>O<sub>7</sub> [and Pb<sub>3</sub>(SbO<sub>4</sub>)<sub>2</sub>]

**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  $1 \times 1 \text{cm}^2$  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  $1 \times 10^{-5}$  and  $1 \times 10^{-6}$  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)  $\text{PbCO}_3$  and (Accession #01909, 01910)  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$

**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,  $\text{CO}_2$ , 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  $\text{CO}_2$ . 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  $1 \times 1 \text{ cm}^2$  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  $-30 \text{ V}$ . Flood gun filament current of 2.35 A. Surface potential was corrected (sample dependent).

**Temp. During Analysis:** 300 K

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

**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:**  $\text{Pb}_3\text{O}_4$

**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  $1 \times 1 \text{ cm}^2$  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  $-30 \text{ V}$ . Flood gun filament current of 2.35 A. Surface potential was corrected (sample dependent).

**Temp. During Analysis:** 300 K

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

**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:**  $\text{PbO}$

**Form:** Ground pigment powder

**History and Significance:** Litharge and massicot are lead monoxide polymorphs with the formula  $\text{PbO}$ , 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  $1 \times 1 \text{ cm}^2$  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  $1 \times 10^{-5}$  and  $1 \times 10^{-6}$  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 ( $\Theta_e$ ):**  $0^\circ$

## ■ 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:**  $\text{Bi}_3^+$

**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:**  $\sim 10$  nA

**Pulsed Beam Current:**  $\sim 0.0004$  nA

**Current Measurement Method:** Faraday cup

**Beam Diameter:**  $\sim 2$   $\mu\text{m}$

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

**Raster Pixel Dimensions:**  $128 \times 128$

**Beam Incident Angle:**  $45^\circ$

**Source-to-Analyzer Angle:**  $45^\circ$

### *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:**  $\text{Ar}_n^+$  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:**  $\sim 10$  nA

**Pulsed Beam Current:** N/A

**Current Measurement Method:** Faraday cup

**Beam Diameter:**  $\sim 50$   $\mu\text{m}$

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

**Raster Pixel Dimensions:** N/A

**Beam Incident Angle:**  $45^\circ$

**Source-to-Analyzer Angle:**  $45^\circ$

## ACKNOWLEDGMENTS

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## 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.

**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

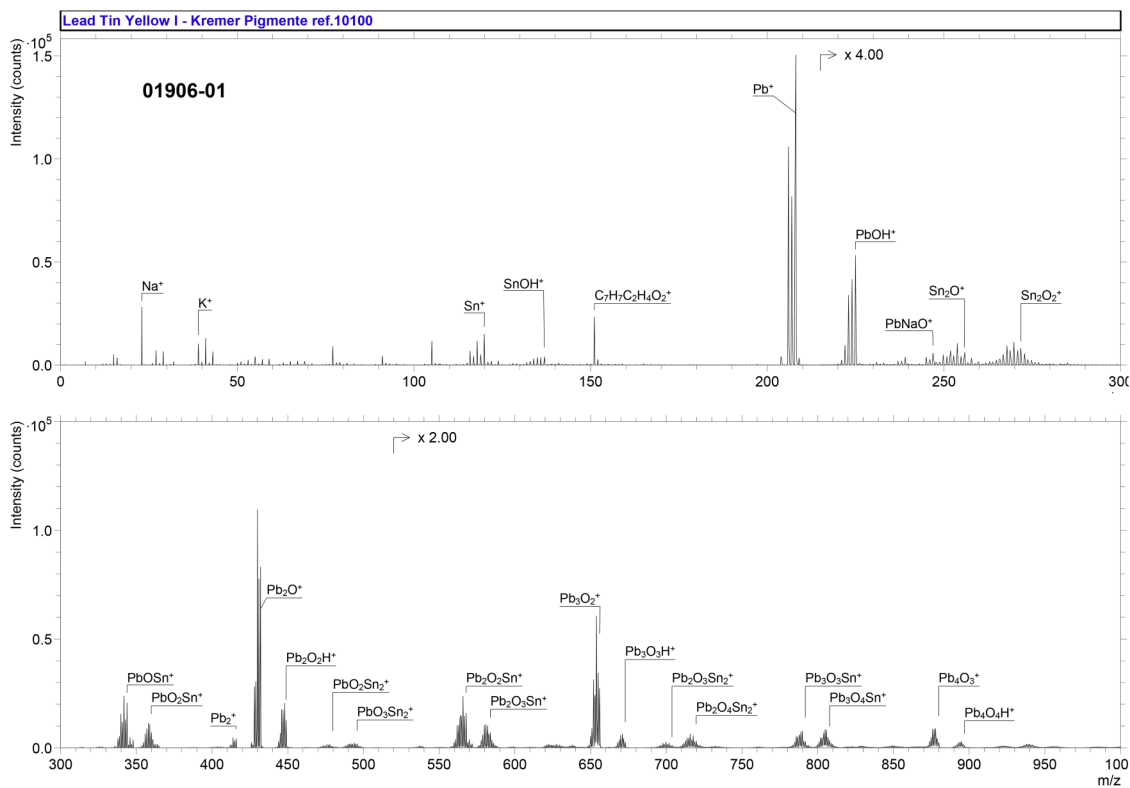
The data that support the findings of this study are available within the article and its supplementary material.

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SPECTRAL FEATURES TABLE

Lead Tin Yellow I—Kremer Pigmente Ref. 10100—Positive polarity				
Spectrum ID #	Mass ( $\Delta m$ ), Da	Species	Peak Assignment	
01906-01	38.964 (19.1)	$K^+$	Impurity	
	119.898 (-27.2)	$Sn^+$	$Pb_2SnO_4$	
	136.906 (8.38)	$SnOH^+$	$Pb_2SnO_4$	
	246.967 (25.9)	$PbNaO^+$	Impurity	
	255.796 (-12.3)	$Sn_2O^+$	$Pb_2SnO_4$	
	271.802 (-30.2)	$Sn_2O_2^+$	$Pb_2SnO_4$	
	343.873 (0.13)	$PbOSn^+$	$Pb_2SnO_4$	
	359.877 (23.5)	$PbO_2Sn^+$	$Pb_2SnO_4$	
	479.793 (46.3)	$PbO_2Sn_2^+$	$Pb_2SnO_4$	
	495.774 (17.1)	$PbO_3Sn_2^+$	$Pb_2SnO_4$	
	567.825 (-34.5)	$Pb_2O_2Sn^+$	$Pb_2SnO_4$	
	583.835 (-8.35)	$Pb_2O_3Sn^+$	$Pb_2SnO_4$	
	703.743 (2.21)	$Pb_2O_3Sn_2^+$	$Pb_2SnO_4$	
	719.750 (17.8)	$Pb_2O_4Sn_2^+$	$Pb_2SnO_4$	
	791.814 (-3.15)	$Pb_3O_3Sn^+$	$Pb_2SnO_4$	
	807.823 (14.2)	$Pb_3O_4Sn^+$	$Pb_2SnO_4$	
	1015.791 (2.59)	$Pb_4O_4Sn^+$	$Pb_2SnO_4$	
	1031.782 (-0.63)	$Pb_4O_5Sn^+$	$Pb_2SnO_4$	



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Accession #:

01906-01

■ Specimen:  
■ Technique:  
Instrument:

Lead Tin Yellow I—Kremer Pigmente Ref. 10100  
SIMS  
IONTOF, TOF SIMS IV

(Continued.)

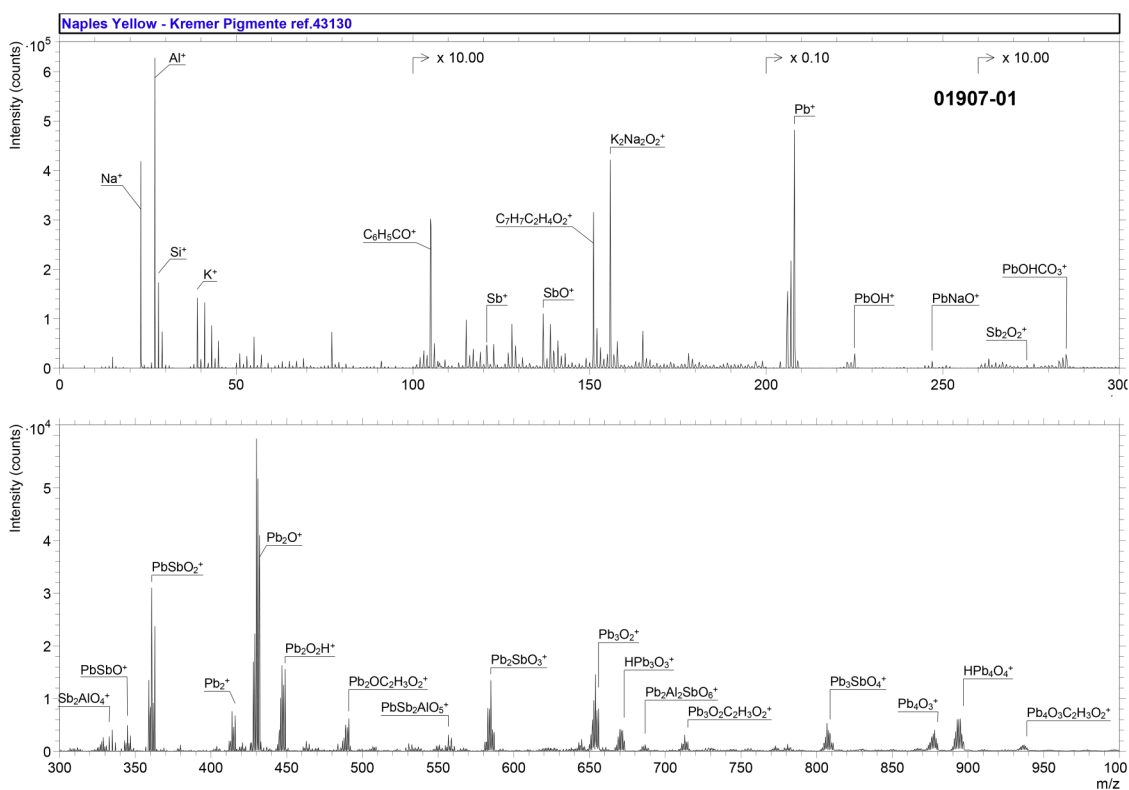
Accession #:	01906-01
Analyzer Type:	Time-of-flight
Analyzer Mass Resolution:	3100 m/Δm
Mass Resolution Determined at:	27 Da
Species Used for Mass Calibration:	Na <sup>+</sup> , Pb <sup>+</sup> , Pb <sub>2</sub> <sup>+</sup> , Pb <sub>2</sub> O <sup>+</sup> , <sup>206</sup> PbPb <sub>2</sub> O <sub>2</sub> <sup>+</sup> , <sup>206</sup> PbPb <sub>3</sub> O <sub>3</sub> <sup>+</sup> , and <sup>206</sup> PbPb <sub>4</sub> O <sub>4</sub> <sup>+</sup>
Specimen Normal-to-Analyzer:	0°
Source-to-Analyzer Angle:	45°
Primary Beam Ion Gun:	LMIG
Primary Ion Species:	Bi <sub>3</sub> <sup>+</sup>
Primary Ion Dose:	4.34 × 10 <sup>11</sup> ion/cm <sup>2</sup>
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:	~2 μm
Beam Raster Size:	250 × 250 μm <sup>2</sup>
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

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Naples Yellow—Kremer Pigmente Ref. 43130—Positive polarity

Spectrum ID #	Mass ( $\Delta m$ ), Da	Species	Peak Assignment
01907-01	26.982 (23.4)	Al <sup>+</sup>	Impurity, likely from the manufacturing process
	27.976 (-32.2)	Si <sup>+</sup>	Impurity, likely from the manufacturing process
	38.965 (36.8)	K <sup>+</sup>	Impurity, likely from the manufacturing process
	120.900 (-25.5)	Sb <sup>+</sup>	Pb <sub>2</sub> Sb <sub>2</sub> O <sub>7</sub> /Pb <sub>3</sub> (SbO <sub>4</sub> ) <sub>2</sub>
	136.901 (22.6)	SbO <sup>+</sup>	Pb <sub>2</sub> Sb <sub>2</sub> O <sub>7</sub> /Pb <sub>3</sub> (SbO <sub>4</sub> ) <sub>2</sub>
	155.895 (-11.0)	K <sub>2</sub> Na <sub>2</sub> O <sub>2</sub> <sup>+</sup>	Impurity, likely from the manufacturing process
	272.802 (18.5)	Sb <sub>2</sub> O <sub>2</sub> <sup>+</sup>	Pb <sub>2</sub> Sb <sub>2</sub> O <sub>7</sub> /Pb <sub>3</sub> (SbO <sub>4</sub> ) <sub>2</sub>
	332.779 (33.2)	Sb <sub>2</sub> AlO <sub>4</sub> <sup>+</sup>	—
	344.883 (24.1)	PbSbO <sup>+</sup>	Pb <sub>2</sub> Sb <sub>2</sub> O <sub>7</sub> /Pb <sub>3</sub> (SbO <sub>4</sub> ) <sub>2</sub>
	360.881 (31.4)	PbSbO <sub>2</sub> <sup>+</sup>	Pb <sub>2</sub> Sb <sub>2</sub> O <sub>7</sub> /Pb <sub>3</sub> (SbO <sub>4</sub> ) <sub>2</sub>
	490.954 (-14.8)	Pb <sub>2</sub> OC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>+</sup>	—
	556.740 (-0.48)	PbSb <sub>2</sub> AlO <sub>5</sub> <sup>+</sup>	—
	584.855 (23.9)	Pb <sub>2</sub> SbO <sub>3</sub> <sup>+</sup>	Pb <sub>2</sub> Sb <sub>2</sub> O <sub>7</sub> /Pb <sub>3</sub> (SbO <sub>4</sub> ) <sub>2</sub>
	686.808 (27.4)	Pb <sub>2</sub> SbAl <sub>2</sub> O <sub>6</sub> <sup>+</sup>	—
	714.920 (-18.0)	Pb <sub>3</sub> O <sub>2</sub> C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>+</sup>	—
	808.828 (18.2)	Pb <sub>3</sub> SbO <sub>4</sub> <sup>+</sup>	Pb <sub>2</sub> Sb <sub>2</sub> O <sub>7</sub> /Pb <sub>3</sub> (SbO <sub>4</sub> ) <sub>2</sub>
938.892 (-12.6)	Pb <sub>4</sub> O <sub>3</sub> C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>+</sup>	—	
1120.893 (24.6)	Pb <sub>5</sub> O <sub>5</sub> H <sup>+</sup>	Pb <sub>2</sub> Sb <sub>2</sub> O <sub>7</sub> /Pb <sub>3</sub> (SbO <sub>4</sub> ) <sub>2</sub>	



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Accession #:

01907-01

■ Specimen:

Naples Yellow—Kremer Pigmente Ref. 43130

■ Technique:

SIMS

Instrument:

IONTOF, TOF SIMS IV

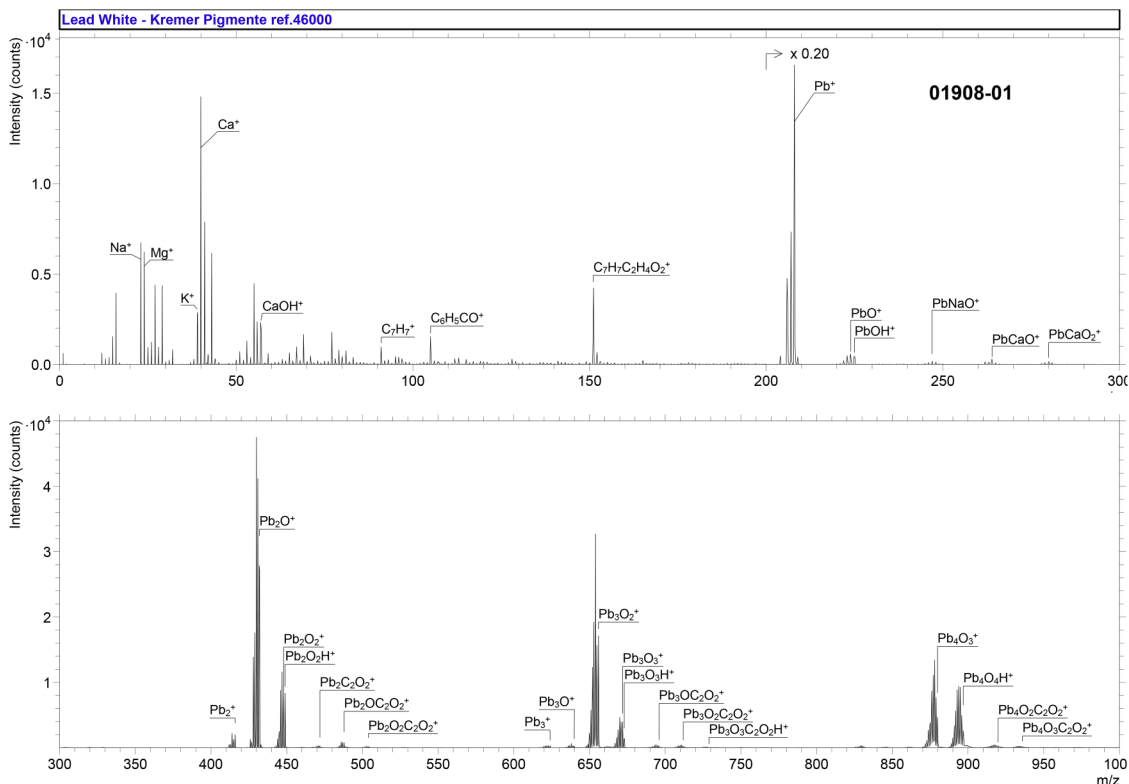
(Continued.)

Accession #:	01907-01
Analyzer Type:	Time-of-flight
Analyzer Mass Resolution:	2600 m/Δm
Mass Resolution Determined at:	27 Da
Species Used for Mass Calibration:	Na <sup>+</sup> , Pb <sup>+</sup> , Pb <sub>2</sub> <sup>+</sup> , Pb <sub>2</sub> O <sup>+</sup> , <sup>206</sup> PbPb <sub>2</sub> O <sub>2</sub> <sup>+</sup> , <sup>206</sup> PbPb <sub>3</sub> O <sub>3</sub> <sup>+</sup> , and <sup>206</sup> PbPb <sub>4</sub> O <sub>4</sub> <sup>+</sup>
Specimen Normal-to-Analyzer:	0°
Source-to-Analyzer Angle:	45°
Primary Beam Ion Gun:	LMIG
Primary Ion Species:	Bi <sub>3</sub> <sup>+</sup>
Primary Ion Dose:	4.34 × 10 <sup>11</sup> ion/cm <sup>2</sup>
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:	~2 μm
Beam Raster Size:	250 × 250 μm <sup>2</sup>
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 <sup>+</sup> (theoretical mass 136.904) and SbO <sup>+</sup> (theoretical mass 136.898)

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Lead White—Kremer Pigmente Ref. 46000—Positive polarity			
Spectrum ID #	Mass ( $\Delta m$ ), Da	Species	Peak Assignment
01908-01	23.984 (−3.22)	Mg <sup>+</sup>	—
	38.965 (38.5)	K <sup>+</sup>	—
	39.962 (−9.51)	Ca <sup>+</sup>	—
	56.966 (17.5)	CaOH <sup>+</sup>	—
	91.057 (25.0)	C <sub>7</sub> H <sub>7</sub> <sup>+</sup>	—
	105.035 (15.2)	C <sub>6</sub> H <sub>5</sub> CO <sup>+</sup>	<i>Phthalate contamination</i>
	151.080 (28.3)	C <sub>7</sub> H <sub>7</sub> (CH <sub>2</sub> O) <sub>2</sub> <sup>+</sup>	—
	223.972 (4.36)	PbO <sup>+</sup>	PbCO <sub>3</sub>
	246.964 (12.5)	PbNaO <sup>+</sup>	—
	263.940 (23.6)	PbCaO <sup>+</sup>	—
	279.931 (7.79)	PbCaO <sub>2</sub> <sup>+</sup>	—
	447.960 (38.0)	Pb <sub>2</sub> O <sub>2</sub> <sup>+</sup>	PbCO <sub>3</sub>
	471.961 (39.1)	Pb <sub>2</sub> (CO) <sub>2</sub> <sup>+</sup>	PbCO <sub>3</sub>
	487.933 (−10.2)	Pb <sub>2</sub> O(CO) <sub>2</sub> <sup>+</sup>	PbCO <sub>3</sub>
	503.914 (−36.4)	Pb <sub>2</sub> O <sub>2</sub> (CO) <sub>2</sub> <sup>+</sup>	PbCO <sub>3</sub>
	623.933 (5.53)	Pb <sub>3</sub> <sup>+</sup>	PbCO <sub>3</sub>
	639.909 (−23.6)	Pb <sub>3</sub> O <sup>+</sup>	PbCO <sub>3</sub>
	671.914 (−0.23)	Pb <sub>3</sub> O <sub>3</sub> <sup>+</sup>	PbCO <sub>3</sub>
	695.898 (−23.7)	Pb <sub>3</sub> O(CO) <sub>2</sub> <sup>+</sup>	PbCO <sub>3</sub>
	711.894 (−21.4)	Pb <sub>3</sub> O <sub>2</sub> (CO) <sub>2</sub> <sup>+</sup>	PbCO <sub>3</sub>
	728.902 (−13.2)	Pb <sub>3</sub> O <sub>3</sub> C <sub>2</sub> O <sub>2</sub> H <sup>+</sup>	PbCO <sub>3</sub>
	919.865 (−22.1)	Pb <sub>4</sub> O <sub>2</sub> (CO) <sub>2</sub> <sup>+</sup>	PbCO <sub>3</sub>
	935.869 (−11.9)	Pb <sub>4</sub> O <sub>3</sub> (CO) <sub>2</sub> <sup>+</sup>	PbCO <sub>3</sub>
	1039.876 (−6.42)	Pb <sub>5</sub> <sup>+</sup>	PbCO <sub>3</sub>
	1120.856 (−8.22)	Pb <sub>5</sub> O <sub>5</sub> H <sup>+</sup>	PbCO <sub>3</sub>
	1327.827 (−4.87)	Pb <sub>6</sub> O <sub>5</sub> <sup>+</sup>	PbCO <sub>3</sub>
1344.832 (−3.10)	Pb <sub>6</sub> O <sub>6</sub> H <sup>+</sup>	PbCO <sub>3</sub>	

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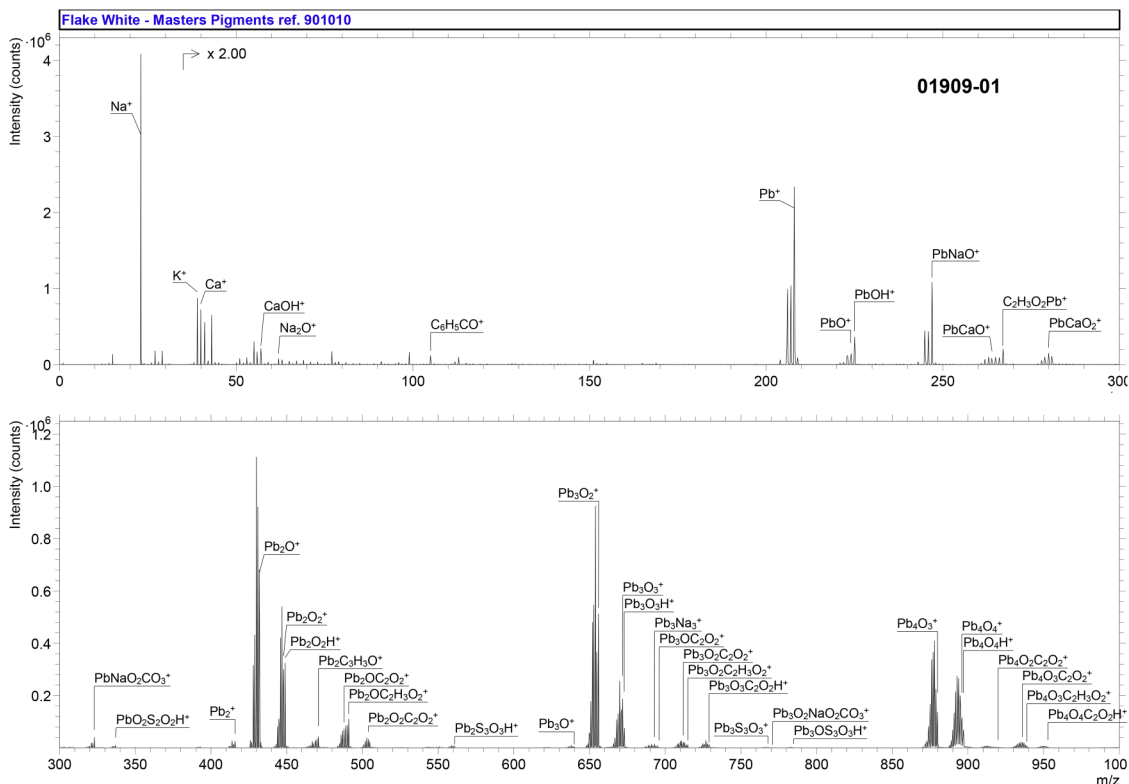


Accession #:	01908-01
■ Specimen:	Lead White—Kremer Pigmente Ref. 46000
■ Technique:	SIMS
Instrument:	IONTOF, TOF SIMS IV
Analyzer Type:	Time-of-flight
Analyzer Mass Resolution:	4000 m/Δm
Mass Resolution Determined at:	27 Da
Species Used for Mass Calibration:	Na <sup>+</sup> , Pb <sup>+</sup> , Pb <sub>2</sub> <sup>+</sup> , Pb <sub>2</sub> O <sup>+</sup> , <sup>206</sup> PbPb <sub>2</sub> O <sub>2</sub> <sup>+</sup> , <sup>206</sup> PbPb <sub>3</sub> O <sub>3</sub> <sup>+</sup> , and <sup>206</sup> PbPb <sub>4</sub> O <sub>4</sub> <sup>+</sup>
Specimen Normal-to-Analyzer:	0°
Source-to-Analyzer Angle:	45°
Primary Beam Ion Gun:	LMIG
Primary Ion Species:	Bi <sub>3</sub> <sup>+</sup>
Primary Ion Dose:	4.37 × 10 <sup>11</sup> ion/cm <sup>2</sup>
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 16 nA
DC Beam Current:	15.7 nA
Beam Diameter:	~2 μm
Beam Raster Size:	250 × 250 μm <sup>2</sup>
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.

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Flake White 10 $\mu$ —Masters Pigments Ref. 901010—Positive polarity			
Spectrum ID #	Mass ( $\Delta$ m), Da	Species	Peak Assignment
01909-01	38.963 (2.82)	K <sup>+</sup>	—
	39.960 (−58.9)	Ca <sup>+</sup>	—
	56.963 (−26.3)	CaOH <sup>+</sup>	—
	61.975 (22.7)	Na <sub>2</sub> O <sup>+</sup>	—
	105.037 (31.7)	C <sub>6</sub> H <sub>5</sub> CO <sup>+</sup>	Phthalate contamination
	223.976 (22.9)	PbO <sup>+</sup>	2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub>
	246.974 (54.7)	PbNaO <sup>+</sup>	—
	263.947 (48.9)	PbCaO <sup>+</sup>	—
	267.006 (62.5)	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> Pb <sup>+</sup>	From lead acetate
	279.938 (34.2)	PbCaO <sub>2</sub> <sup>+</sup>	—
	322.951 (33.3)	PbNaO <sub>2</sub> CO <sub>3</sub> <sup>+</sup>	—
	336.895 (−38.7)	PbS <sub>2</sub> O <sub>4</sub> H <sup>+</sup>	—
	447.950 (16.3)	Pb <sub>2</sub> O <sub>2</sub> <sup>+</sup>	2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub>
	470.942 (−61.1)	Pb <sub>2</sub> C <sub>3</sub> H <sub>3</sub> O <sup>+</sup>	2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub>
	471.941 (−3.48)	Pb <sub>2</sub> (CO) <sub>2</sub> <sup>+</sup>	2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub>
	487.934 (−7.58)	Pb <sub>2</sub> O(CO) <sub>2</sub> <sup>+</sup>	2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub>
	490.965 (8.80)	Pb <sub>2</sub> OC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>+</sup>	From lead acetate
	503.903 (−59.1)	Pb <sub>2</sub> O <sub>2</sub> (CO) <sub>2</sub> <sup>+</sup>	2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub>
	560.835 (−47.3)	Pb <sub>2</sub> S <sub>3</sub> O <sub>3</sub> H <sup>+</sup>	—
	623.922 (−12.5)	Pb <sub>3</sub> <sup>+</sup>	2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub>
	639.920 (−6.39)	Pb <sub>3</sub> O <sup>+</sup>	2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub>
	671.920 (9.20)	Pb <sub>3</sub> O <sub>3</sub> <sup>+</sup>	2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub>
	692.906 (10.2)	Pb <sub>3</sub> Na <sub>3</sub> <sup>+</sup>	—
	694.914 (−41.9)	Pb <sub>3</sub> OC <sub>3</sub> H <sub>3</sub> O <sup>+</sup>	2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub>
	695.907 (−10.4)	Pb <sub>3</sub> O(CO) <sub>2</sub> <sup>+</sup>	2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub>
	711.901 (−11.3)	Pb <sub>3</sub> O <sub>2</sub> (CO) <sub>2</sub> <sup>+</sup>	2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub>
	714.938 (7.74)	Pb <sub>3</sub> O <sub>2</sub> C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>+</sup>	From lead acetate
	728.876 (−48.8)	Pb <sub>3</sub> O <sub>3</sub> (CO) <sub>2</sub> H <sup>+</sup>	2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub>
	767.842 (14.8)	Pb <sub>3</sub> S <sub>3</sub> O <sub>3</sub> <sup>+</sup>	—
	770.874 (−12.3)	Pb <sub>3</sub> O <sub>2</sub> NaO <sub>2</sub> CO <sub>3</sub> <sup>+</sup>	—
	784.822 (−13.7)	Pb <sub>3</sub> OS <sub>3</sub> O <sub>3</sub> H <sup>+</sup>	—
	895.896 (11.4)	Pb <sub>4</sub> O <sub>4</sub> <sup>+</sup>	2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub>
	919.879 (−6.78)	Pb <sub>4</sub> O <sub>2</sub> (CO) <sub>2</sub> <sup>+</sup>	2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub>
	935.893 (13.5)	Pb <sub>4</sub> O <sub>3</sub> (CO) <sub>2</sub> <sup>+</sup>	2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub>
	938.923 (19.8)	Pb <sub>4</sub> O <sub>3</sub> C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>+</sup>	From lead acetate
	952.844 (−41.6)	Pb <sub>4</sub> O <sub>4</sub> (CO) <sub>2</sub> H <sup>+</sup>	2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub>
1119.877 (17.9)	Pb <sub>5</sub> O <sub>5</sub> <sup>+</sup>	2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub>	
1120.876 (10.1)	Pb <sub>5</sub> O <sub>5</sub> H <sup>+</sup>	2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub>	
1327.849 (11.5)	Pb <sub>6</sub> O <sub>6</sub> <sup>+</sup>	2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub>	
1343.857 (20.7)	Pb <sub>6</sub> O <sub>6</sub> <sup>+</sup>	2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub>	
1344.862 (19.4)	Pb <sub>6</sub> O <sub>6</sub> H <sup>+</sup>	2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub>	

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Accession #:

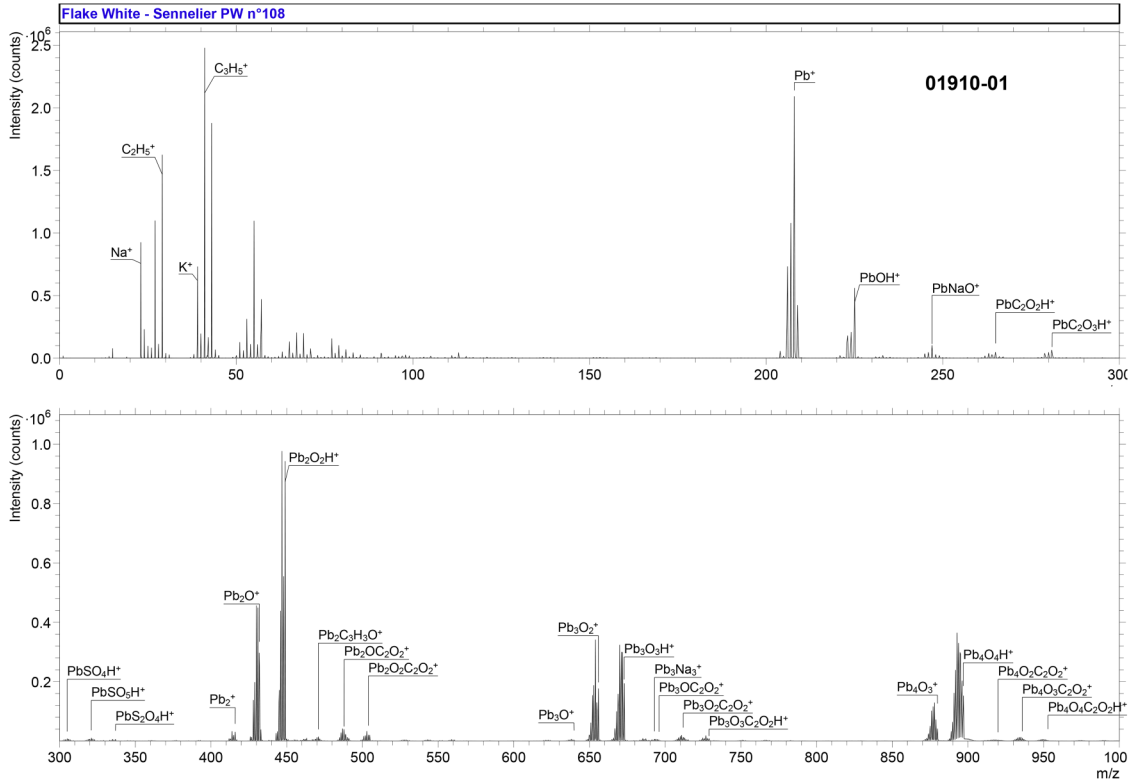
01909-01

■ Specimen:	Flake White 10 $\mu$ —Masters Pigments Ref. 901010
■ Technique:	SIMS
Instrument:	IONTOF, TOF SIMS IV
Analyzer Type:	Time-of-flight
Analyzer Mass Resolution:	4400 m/ $\Delta$ m
Mass Resolution Determined at:	27 Da
Species Used for Mass Calibration:	Na <sup>+</sup> , Pb <sup>+</sup> , Pb <sub>2</sub> <sup>+</sup> , Pb <sub>2</sub> O <sup>+</sup> , <sup>206</sup> PbPb <sub>2</sub> O <sub>2</sub> <sup>+</sup> , <sup>206</sup> PbPb <sub>3</sub> O <sub>3</sub> <sup>+</sup> , and <sup>206</sup> PbPb <sub>4</sub> O <sub>4</sub> <sup>+</sup>
Specimen Normal-to-Analyzer:	0°
Source-to-Analyzer Angle:	45°
Primary Beam Ion Gun:	LMIG
Primary Ion Species:	Bi <sub>3</sub> <sup>+</sup>
Primary Ion Dose:	4.37 × 10 <sup>11</sup> ion/cm <sup>2</sup>
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:	0.000 38 nA
DC Beam Current:	1.9 nA
Beam Diameter:	~2 $\mu$ m
Beam Raster Size:	200 × 200 $\mu$ m <sup>2</sup>
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:	Assignments were refined using isotopic patterns.

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Flake White—Sennelier PW No. 108— Positive polarity			
Spectrum ID #	Mass ( $\Delta m$ ), Da	Species	Peak Assignment
01910-01	38.965 (37.1)	$K^+$	—
	246.974 (54.8)	$PbNaO^+$	—
	264.979 (20.1)	$PbC_2O_2H^+$	$2PbCO_3 \cdot Pb(OH)_2$
	280.952 (−58.2)	$PbC_2O_3H^+$	$2PbCO_3 \cdot Pb(OH)_2$
	304.949 (43.6)	$PbSO_4H^+$	—
	320.928 (−8.09)	$PbSO_5H^+$	—
	336.898 (−28.9)	$PbS_2O_4H^+$	—
	470.941 (−63.6)	$Pb_2C_3H_3O^+$	$2PbCO_3 \cdot Pb(OH)_2$
	471.927 (−32.2)	$Pb_2(CO)_2^+$	—
	487.926 (−22.8)	$Pb_2O(CO)_2^+$	$2PbCO_3 \cdot Pb(OH)_2$
	503.910 (−44.4)	$Pb_2O_2(CO)_2^+$	$2PbCO_3 \cdot Pb(OH)_2$
	528.927 (36.7)	$Pb_2O_2SO_3H^+$	—
	544.890 (−22.6)	$Pb_2O_3SO_3H^+$	—
	560.841 (−36.8)	$Pb_2S_3O_3H^+$	—
	639.917 (−12.0)	$Pb_3O^+$	$2PbCO_3 \cdot Pb(OH)_2$
	692.893 (−8.49)	$Pb_3Na_3^+$	—
	694.901 (−59.7)	$Pb_3OC_3H_3O^+$	$2PbCO_3 \cdot Pb(OH)_2$
	695.889 (−35.8)	$Pb_3O(CO)_2^+$	$2PbCO_3 \cdot Pb(OH)_2$
	711.894 (−21.1)	$Pb_3O_2(CO)_2^+$	$2PbCO_3 \cdot Pb(OH)_2$
	728.886 (−35.4)	$Pb_3O_3(CO)_2H^+$	$2PbCO_3 \cdot Pb(OH)_2$
	752.878 (−1.19)	$Pb_3O_3SO_3H^+$	—
	767.842 (15.6)	$Pb_3S_3O_3^+$	—
	784.827 (−7.91)	$Pb_3OS_3O_3H^+$	—
	919.868 (−19.8)	$Pb_4O_2(CO)_2^+$	$2PbCO_3 \cdot Pb(OH)_2$
	935.859 (−23.2)	$Pb_4O_3(CO)_2^+$	$2PbCO_3 \cdot Pb(OH)_2$
	952.846 (−39.0)	$Pb_4O_4(CO)_2H^+$	$2PbCO_3 \cdot Pb(OH)_2$
	1120.873 (7.40)	$Pb_5O_5H^+$	$2PbCO_3 \cdot Pb(OH)_2$
	1327.834 (−0.10)	$Pb_6O_5^+$	$2PbCO_3 \cdot Pb(OH)_2$
	1344.856 (14.8)	$Pb_6O_6H^+$	$2PbCO_3 \cdot Pb(OH)_2$

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Accession #:

01910-01

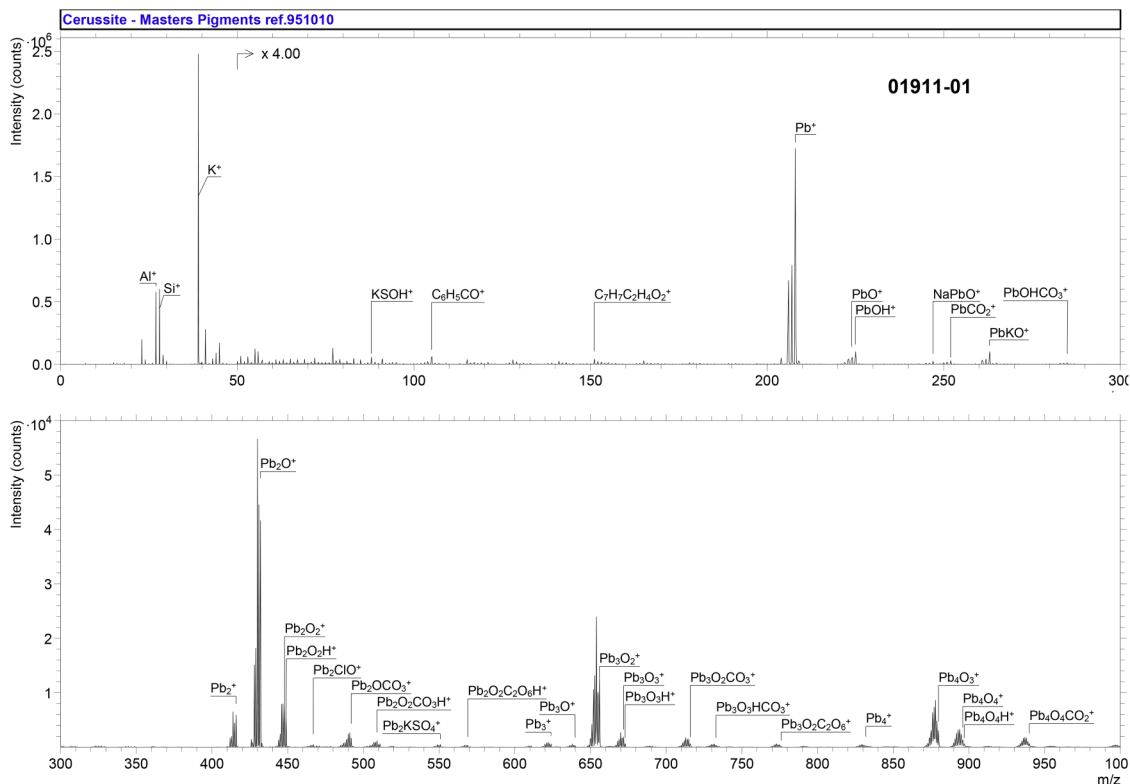
<p>■ Specimen:          ■ Technique:          Instrument:          Analyzer Type:          Analyzer Mass Resolution:          Mass Resolution Determined at:          Species Used for Mass Calibration:          Specimen Normal-to-Analyzer:          Source-to-Analyzer Angle:          Primary Beam Ion Gun:          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>Flake White—Sennelier PW No. 108          SIMS          IONTOF, TOF SIMS IV          Time-of-flight          3500 m/Δm          27 Da  <math>\text{Na}^+</math>, <math>\text{Pb}^+</math>, <math>\text{Pb}_2^+</math>, <math>\text{Pb}_2\text{O}^+</math>, <math>^{206}\text{PbPb}_2\text{O}_2^+</math>, <math>^{206}\text{PbPb}_3\text{O}_3^+</math>, and <math>^{206}\text{PbPb}_4\text{O}_4^+</math>          0°          45°          LMIG  <math>\text{Bi}_3^+</math>  <math>4.37 \times 10^{11}</math> ion/cm<sup>2</sup>          0.8–1.2 ns          8.3 kHz          25 000 eV          0.00038 nA          1.9 nA          ~2 μm          200 × 200 μm<sup>2</sup>          45°          Positive          0 Da          1995 Da          Yes          161 s          None</p>
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Cerussite—Masters Pigments Ref. 951010—Positive polarity			
Spectrum ID #	Mass ( $\Delta m$ ), Da	Species	Peak Assignment
01911-01	26.981 (0.75)	Al <sup>+</sup>	—
	27.975 (−40.3)	Si <sup>+</sup>	—
	38.965 (57.4)	K <sup>+</sup>	—
	87.939 (13.3)	KSOH <sup>+</sup>	—
	105.037 (37.2)	C <sub>6</sub> H <sub>5</sub> CO <sup>+</sup>	<i>Phthalate contamination</i>
	151.080 (31.4)	C <sub>7</sub> H <sub>7</sub> (CH <sub>2</sub> O) <sub>2</sub> <sup>+</sup>	—
	223.978 (30.4)	PbO <sup>+</sup>	PbCO <sub>3</sub>
	246.968 (28.2)	PbONa <sup>+</sup>	—
	251.958 (−33.2)	PbCO <sub>2</sub> <sup>+</sup>	PbCO <sub>3</sub>
	262.944 (35.3)	PbOK <sup>+</sup>	—
	284.965 (6.59)	PbOHCO <sub>3</sub> <sup>+</sup>	PbCO <sub>3</sub>
	447.957 (31.9)	Pb <sub>2</sub> O <sub>2</sub> <sup>+</sup>	PbCO <sub>3</sub>
	466.935 (39.8)	Pb <sub>2</sub> ClO <sup>+</sup>	—
	491.950 (36.3)	Pb <sub>2</sub> OCO <sub>3</sub> <sup>+</sup>	PbCO <sub>3</sub>
	508.951 (30.3)	Pb <sub>2</sub> O <sub>2</sub> CO <sub>3</sub> H <sup>+</sup>	PbCO <sub>3</sub>
	550.890 (38.9)	Pb <sub>2</sub> KSO <sub>4</sub> <sup>+</sup>	—
	568.903 (−28.9)	Pb <sub>2</sub> O <sub>2</sub> C <sub>2</sub> O <sub>6</sub> H <sup>+</sup>	PbCO <sub>3</sub>
	623.933 (6.06)	Pb <sub>3</sub> <sup>+</sup>	PbCO <sub>3</sub>
	639.914 (−16.8)	Pb <sub>3</sub> O <sup>+</sup>	PbCO <sub>3</sub>
	671.922 (11.9)	Pb <sub>3</sub> O <sub>3</sub> <sup>+</sup>	PbCO <sub>3</sub>
	715.923 (26.3)	Pb <sub>3</sub> O <sub>2</sub> CO <sub>3</sub> <sup>+</sup>	PbCO <sub>3</sub>
	732.925 (25.2)	Pb <sub>3</sub> O <sub>3</sub> HCO <sub>3</sub> <sup>+</sup>	PbCO <sub>3</sub>
	775.922 (42.9)	Pb <sub>3</sub> O <sub>2</sub> C <sub>2</sub> O <sub>6</sub> <sup>+</sup>	PbCO <sub>3</sub>
	895.898 (13.6)	Pb <sub>4</sub> O <sub>4</sub> <sup>+</sup>	PbCO <sub>3</sub>
	939.888 (13.8)	Pb <sub>4</sub> O <sub>4</sub> CO <sub>2</sub> <sup>+</sup>	PbCO <sub>3</sub>
	1327.847 (10.2)	Pb <sub>6</sub> O <sub>5</sub> <sup>+</sup>	PbCO <sub>3</sub>

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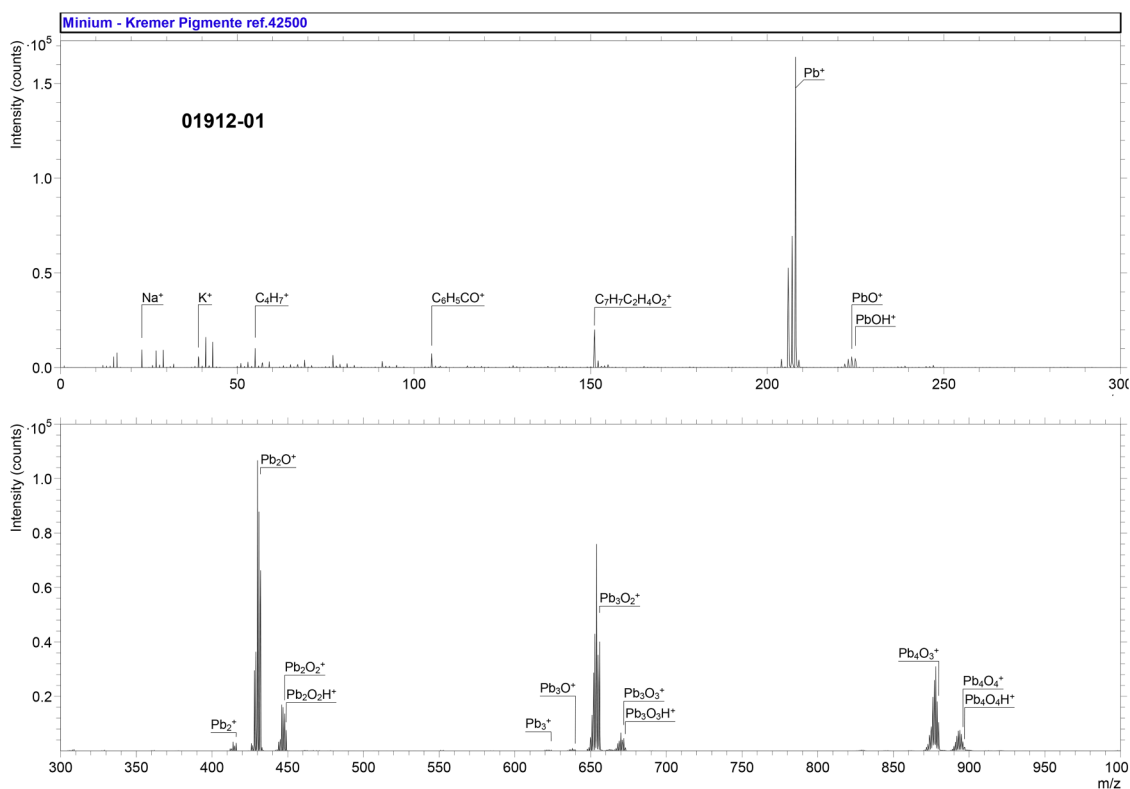
Accession #:

01911-01

■ Specimen:	Cerussite—Masters Pigments Ref. 951010
■ Technique:	SIMS
Instrument:	IONTOF, TOF SIMS IV
Analyzer Type:	Time-of-flight
Analyzer Mass Resolution:	2300 m/Δm
Mass Resolution Determined at:	28 Da
Species Used for Mass Calibration:	Na <sup>+</sup> , Pb <sup>+</sup> , Pb <sub>2</sub> <sup>+</sup> , Pb <sub>2</sub> O <sup>+</sup> , <sup>206</sup> PbPb <sub>2</sub> O <sub>2</sub> <sup>+</sup> , <sup>206</sup> PbPb <sub>3</sub> O <sub>3</sub> <sup>+</sup> , and <sup>206</sup> PbPb <sub>4</sub> O <sub>4</sub> <sup>+</sup>
Specimen Normal-to-Analyzer:	0°
Source-to-Analyzer Angle:	45°
Primary Beam Ion Gun:	LMIG
Primary Ion Species:	Bi <sub>3</sub> <sup>+</sup>
Primary Ion Dose:	4.35 × 10 <sup>11</sup> ion/cm <sup>2</sup>
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:	~2 μm
Beam Raster Size:	250 × 250 μm <sup>2</sup>
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

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Minium—Kremer Pigmente Ref. 42500—Positive polarity			
Spectrum ID #	Mass ( $\Delta m$ ), Da	Species	Peak Assignment
01912-01	38.965 (51.4)	$K^+$	—
	55.058 (58.6)	$C_4H_7^+$	—
	91.058 (37.2)	$C_7H_7^+$	—
	105.037 (37.2)	$C_6H_5CO^+$	Phthalate contamination
	151.079 (26.4)	$C_7H_7(CH_2O)_2^+$	—
	223.973 (10.8)	$PbO^+$	$Pb_3O_4$
	447.961 (40.5)	$Pb_2O_2^+$	$Pb_3O_4$
	623.928 (-3.03)	$Pb_3^+$	$Pb_3O_4$
	639.924 (-0.56)	$Pb_3O^+$	$Pb_3O_4$
	671.921 (10.4)	$Pb_3O_3^+$	$Pb_3O_4$
	895.901 (16.8)	$Pb_4O_4^+$	$Pb_3O_4$
	1119.892 (31.1)	$Pb_5O_5^+$	$Pb_3O_4$
	1120.903 (33.6)	$Pb_5O_5H^+$	$Pb_3O_4$
	1327.837 (2.69)	$Pb_6O_6^+$	$Pb_3O_4$



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<b>Accession #:</b>	<b>01912-01</b>
<b>Specimen:</b>	Minium—Kremer Pigmente Ref. 42500
<b>Technique:</b>	SIMS
<b>Instrument:</b>	IONTOF, TOF SIMS IV
<b>Analyzer Type:</b>	Time-of-flight
<b>Analyzer Mass Resolution:</b>	3900 m/ $\Delta m$

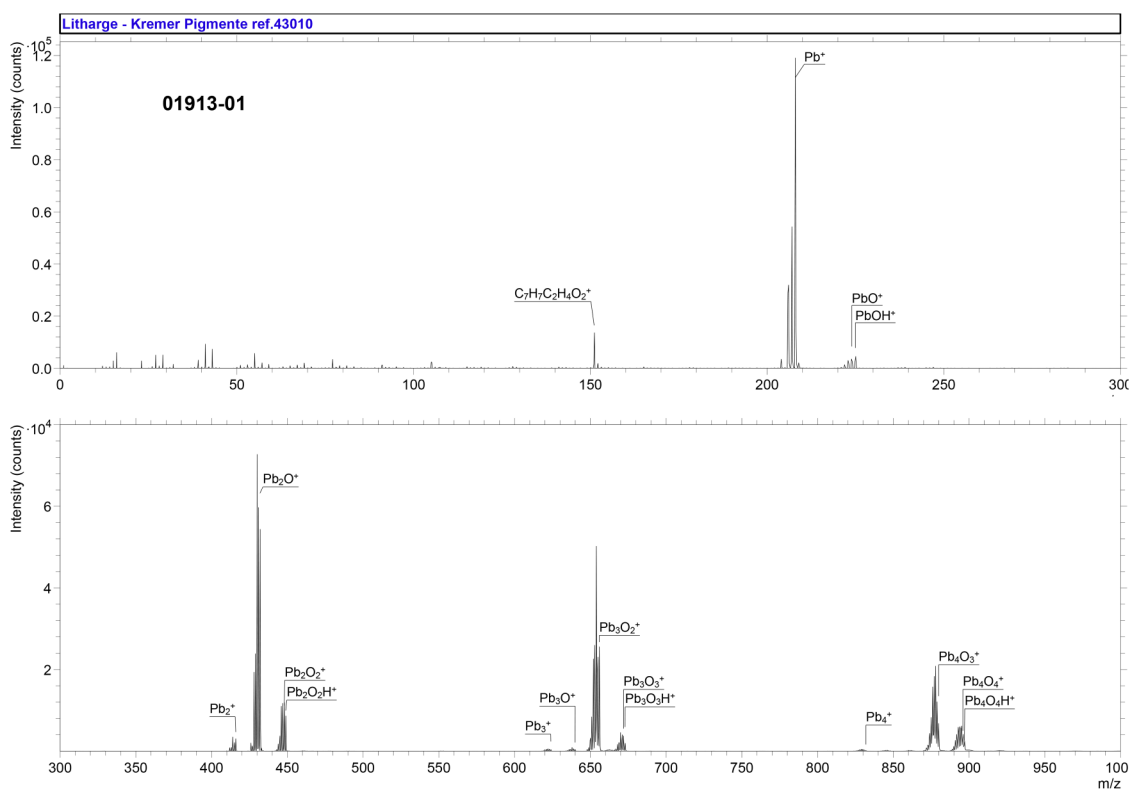
(Continued.)

Accession #:	01912-01
Mass Resolution Determined at:	27 Da
Species Used for Mass Calibration:	Na <sup>+</sup> , Pb <sup>+</sup> , Pb <sub>2</sub> <sup>+</sup> , Pb <sub>2</sub> O <sup>+</sup> , <sup>206</sup> PbPb <sub>2</sub> O <sub>2</sub> <sup>+</sup> , <sup>206</sup> PbPb <sub>3</sub> O <sub>3</sub> <sup>+</sup> , and <sup>206</sup> PbPb <sub>4</sub> O <sub>4</sub> <sup>+</sup>
Specimen Normal-to-Analyzer:	0°
Source-to-Analyzer Angle:	45°
Primary Beam Ion Gun:	LMIG
Primary Ion Species:	Bi <sub>3</sub> <sup>+</sup>
Primary Ion Dose:	4.35 × 10 <sup>11</sup> ion/cm <sup>2</sup>
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:	~2 μm
Beam Raster Size:	250 × 250 μm <sup>2</sup>
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

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Litharge—Kremer Pigmente Ref. 43010—Positive polarity

Spectrum ID #	Mass ( $\Delta m$ ), Da	Species	Peak Assignment
01913-01	151.083 (56.4)	$C_7H_7(CH_2O)_2^+$	—
	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)	$Pb_3O^+$	PbO
	671.939 (37.1)	$Pb_3O_3^+$	PbO
	1039.868 (−14.5)	$Pb_5^+$	PbO
	1120.876 (9.39)	$Pb_5O_5H^+$	PbO



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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/ $\Delta m$
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:	$Bi_3^+$

(Continued.)

Accession #:	01913-01
Primary Ion Dose:	$4.35 \times 10^{11}$ ion/cm <sup>2</sup>
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:	~2 μm
Beam Raster Size:	250 × 250 μm <sup>2</sup>
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

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**SPECTRAL FEATURES TABLE (peaks appearing in all spectra)**

Spectrum ID #	Mass ( $\Delta m$ ), Da	Species	Peak Assignment
All	22.99 (16.6)	Na <sup>+</sup>	—
...	207.98 (9.1)	Pb <sup>+</sup>	All lead-containing pigments
...	224.98 (18.1)	PbOH <sup>+</sup>	All lead-containing pigments
...	415.95 (16.3)	Pb <sub>2</sub> <sup>+</sup>	All lead-containing pigments
...	431.96 (19.9)	Pb <sub>2</sub> O <sup>+</sup>	All lead-containing pigments
...	448.97 (36.2)	Pb <sub>2</sub> O <sub>2</sub> H <sup>+</sup>	All lead-containing pigments
...	655.92 (4.2)	Pb <sub>3</sub> O <sub>2</sub> <sup>+</sup>	All lead-containing pigments
...	672.93 (9.3)	Pb <sub>3</sub> O <sub>3</sub> H <sup>+</sup>	All lead-containing pigments
...	879.89 (8.1)	Pb <sub>4</sub> O <sub>3</sub> <sup>+</sup>	All lead-containing pigments
...	896.89 (17.6)	Pb <sub>4</sub> O <sub>4</sub> H <sup>+</sup>	All lead-containing pigments
...	1103.87 (3.1)	Pb <sub>5</sub> O <sub>4</sub> <sup>+</sup>	All lead-containing pigments

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