“Identification and quantification of metals explored by ultra-high resolution MALDI FTICR mass spectrometry”

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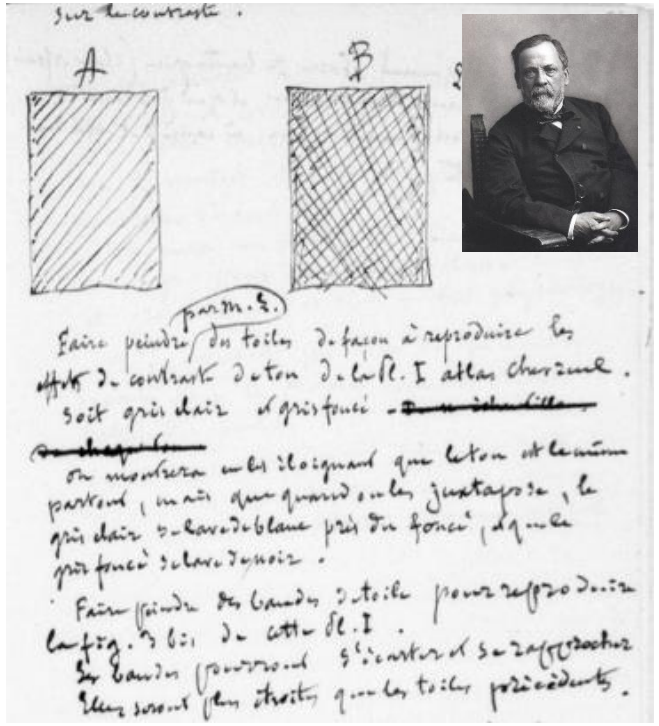
Miniaturization for Synthesis, Analysis & Proteomics USR 3290

EU_FT-ICR_MS

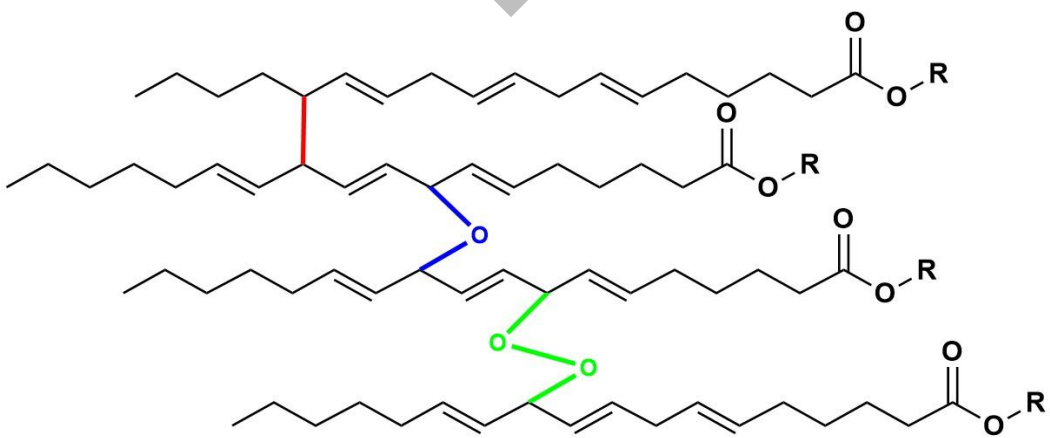
*December 13th 2022 - **University of Lille, FST***

Collaboration between the Lebanese University and University of Lille

The role of metals in the siccativation process



Linseed oil + metal + O_2



- Louis Pasteur - 19th century

First scientific study of driers

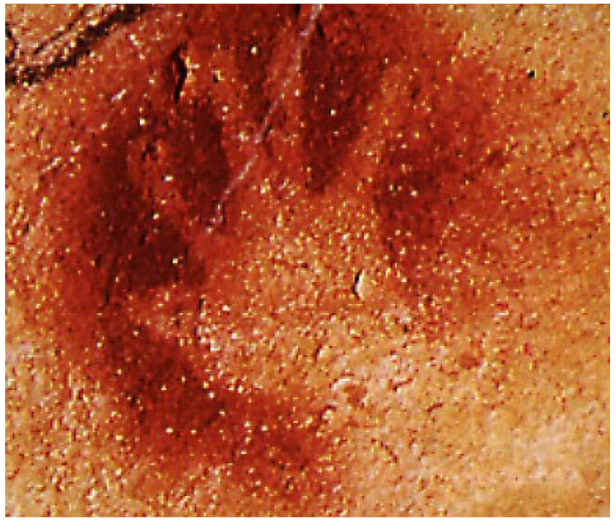
- Siccativation of oil-based paint
  → Formation of a metal dependent cross-linked polymer network

Pallot-Frossard, Isabelle. *L'Actualité chimique*, **2007** 312-13: 6-9, Sciences and conservation of cultural heritage, or the lessons of Pasteur
Louis Pasteur. Papiers. I — Registres de laboratoire et cahiers divers. CX-CXXII Cours professés par Pasteur à l'Ecole des Beaux-Arts https://gallica.bnf.fr/ark:/12148/btv1b9080166m?rk=21459;2

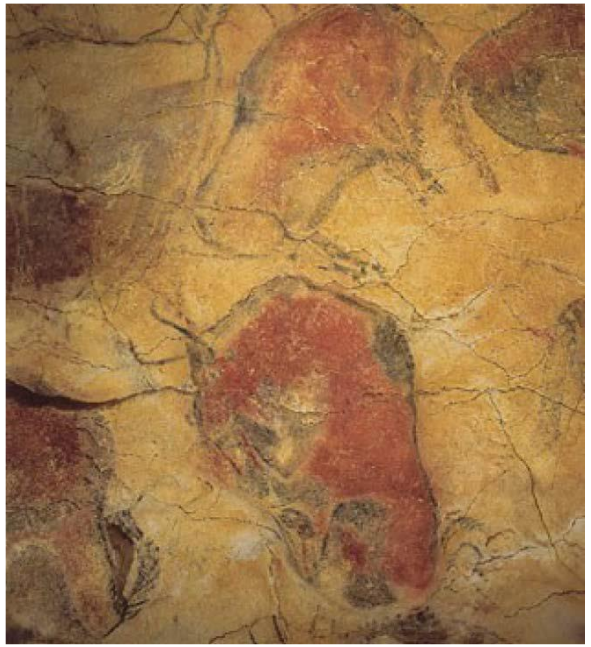
The origin of pigments

1. Earth pigments — Ochres, siennas, umbers
2. Traditional pigments — Metal based pigments
3. Modern pigments — Organic pigments

- Ultra-high resolution FT-ICR mass spectrometry MSAP Laboratory



Hand stencil from the cave at Avignon, France.



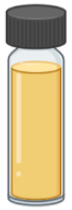
Paintings of bison in the Altamira Caves, Spain.

Barnett, J. R., Miller, S., & Pearce, E. **2006**. Colour and art: A brief history of pigments. *Optics & Laser Technology*, *38*(4-6), 445-453.

Analytical protocol

9 analytical grade metal solutions:
Co(II), Cu(II), Fe(II), Fe(III), Mn(II), Pb(II), Ti(IV), Zn(II), Zr(IV)

+ *N,N*'-bis(salicylidene)-1,2- phenylenediamine



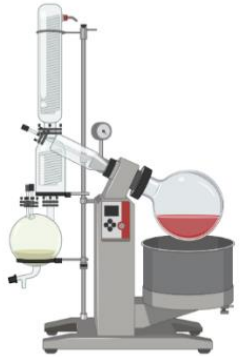
Solution:
Chelating agent in AcN
+metal in H_2O
for **30 minutes**

Column:
3 mL Superclean™
LC C18 SPE 500 mg

Activation:
2 mL of AcN
2 mL of H_2O

Washing:
4 mL of H_2O

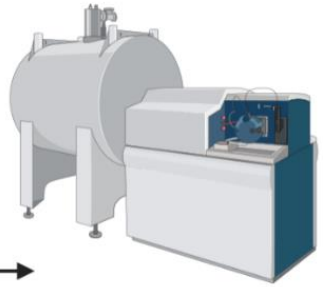
Elution:
6 mL of MeOH

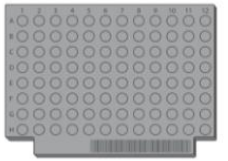


Rotavapor:
Solvent evaporation

Recovery:
50 µL of AcN

Matrix:
10 mg of HCCA
700:300:1 AcN:Water:TFA



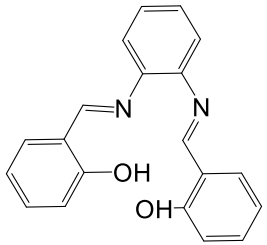


Spotting:
0.5 µL of sample
0.5 µLof matrix

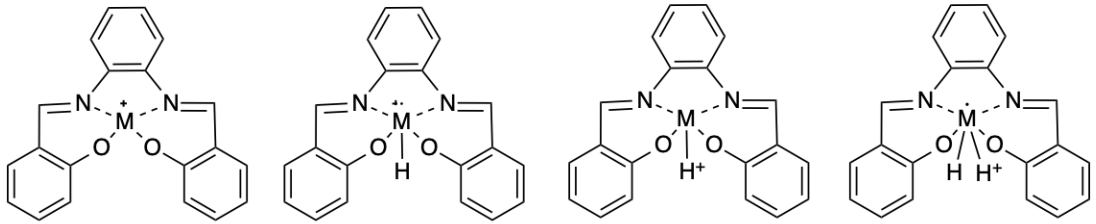
Optimized analysis parameters

Optimized SPE extraction

Detection and speciation of model metal salts



N,N′-Bis(salicylidene)-1,2-phenylenediamine (Salen A)

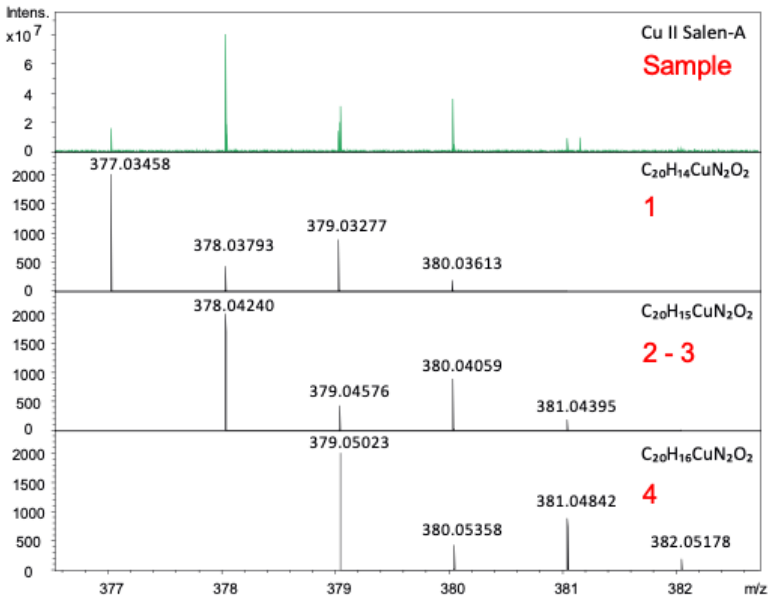


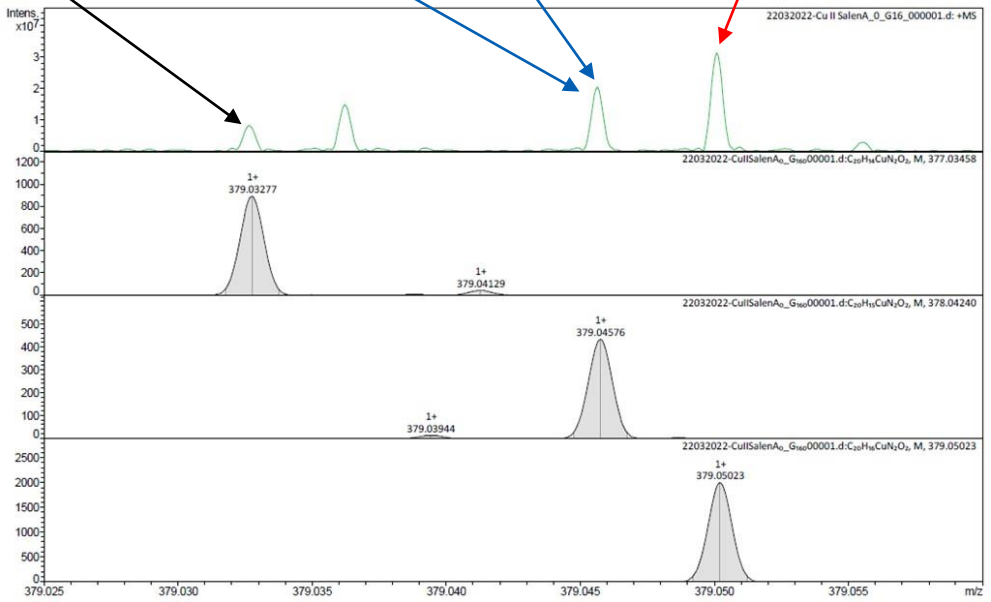
1 Oxidized specie $C_{20}H_{14}M^{3+}N_2O_2$

2 Radical specie $C_{20}H_{15}M^{3+}N_2O_2$

3 Protonated specie $C_{20}H_{15}M^{2+}N_2O_2$

4 Radical pronated specie $C_{20}H_{16}M^{2+}N_2O_2$



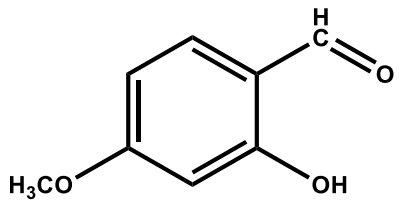


Zoom on Cu(II)

Metal	Complex
Fe(II)	✓
Fe(III)	✓
Co(II)	✓
Mn(II)	✓
Zr(IV)[(a)]	✓
Cu(II)	✓
Ti(IV)	×
Pb(II)	✓
Zn(II)	×

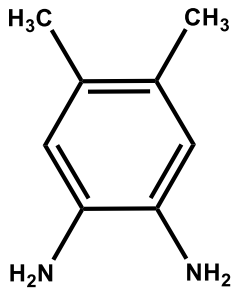
(a) Doubly chelated complex

Synthesis of Salen M



2-hydroxy-4-methoxybenzaldehyde

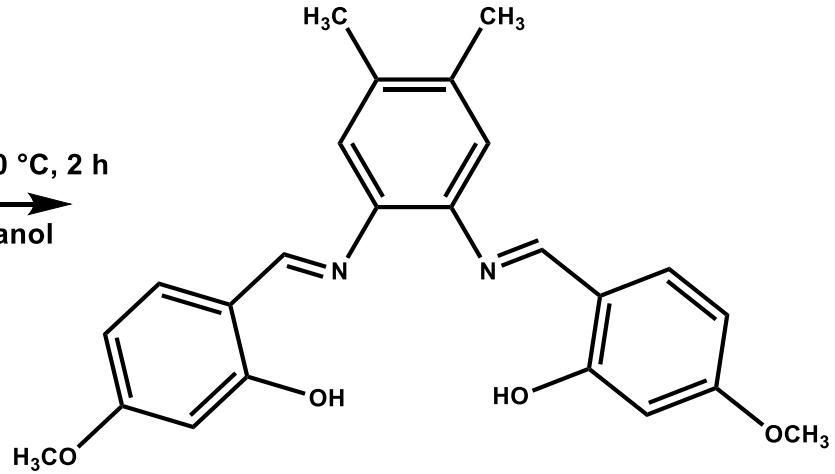
+



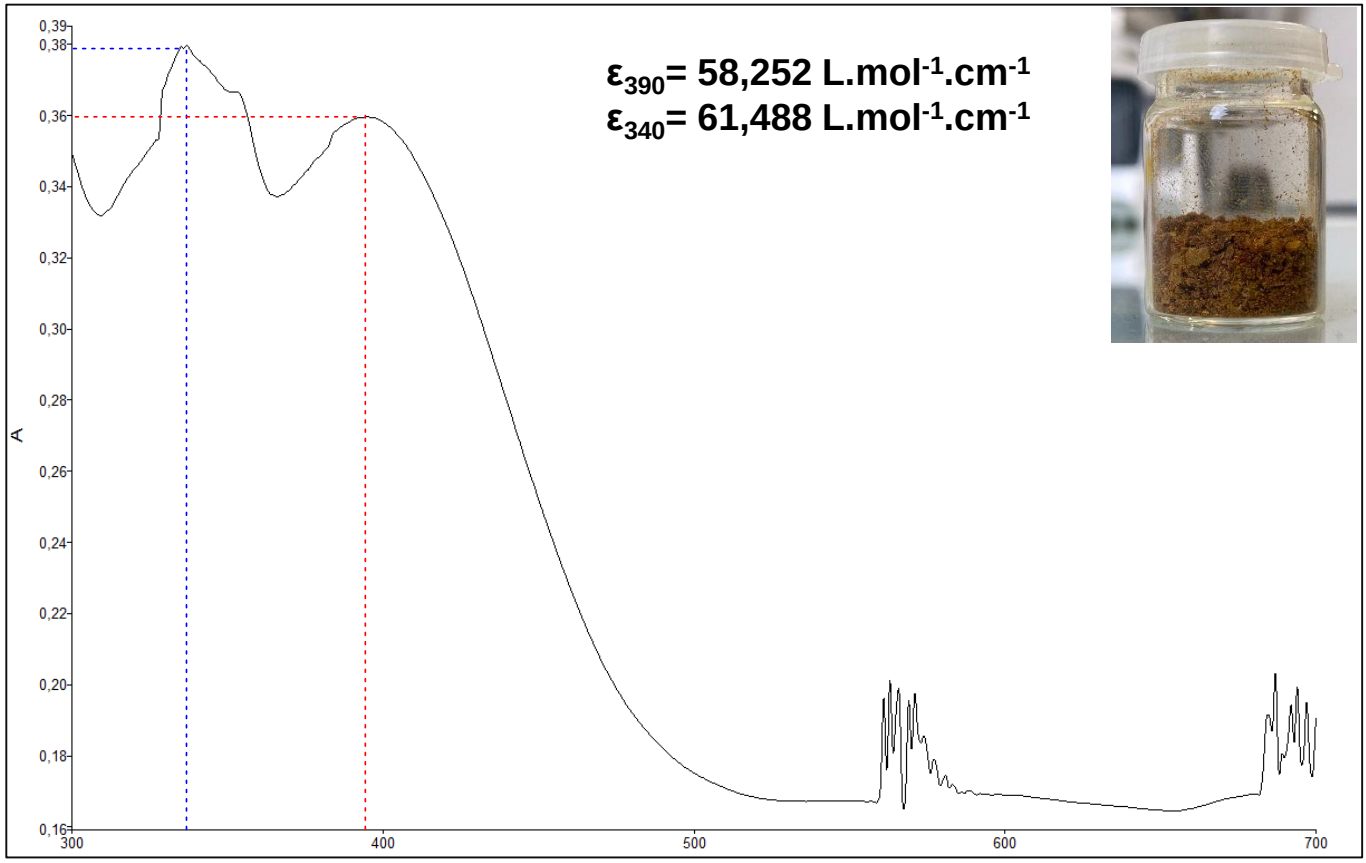
4,5-dimethyl-1,2-phenylenediamine

Reflux, 60 °C, 2 h

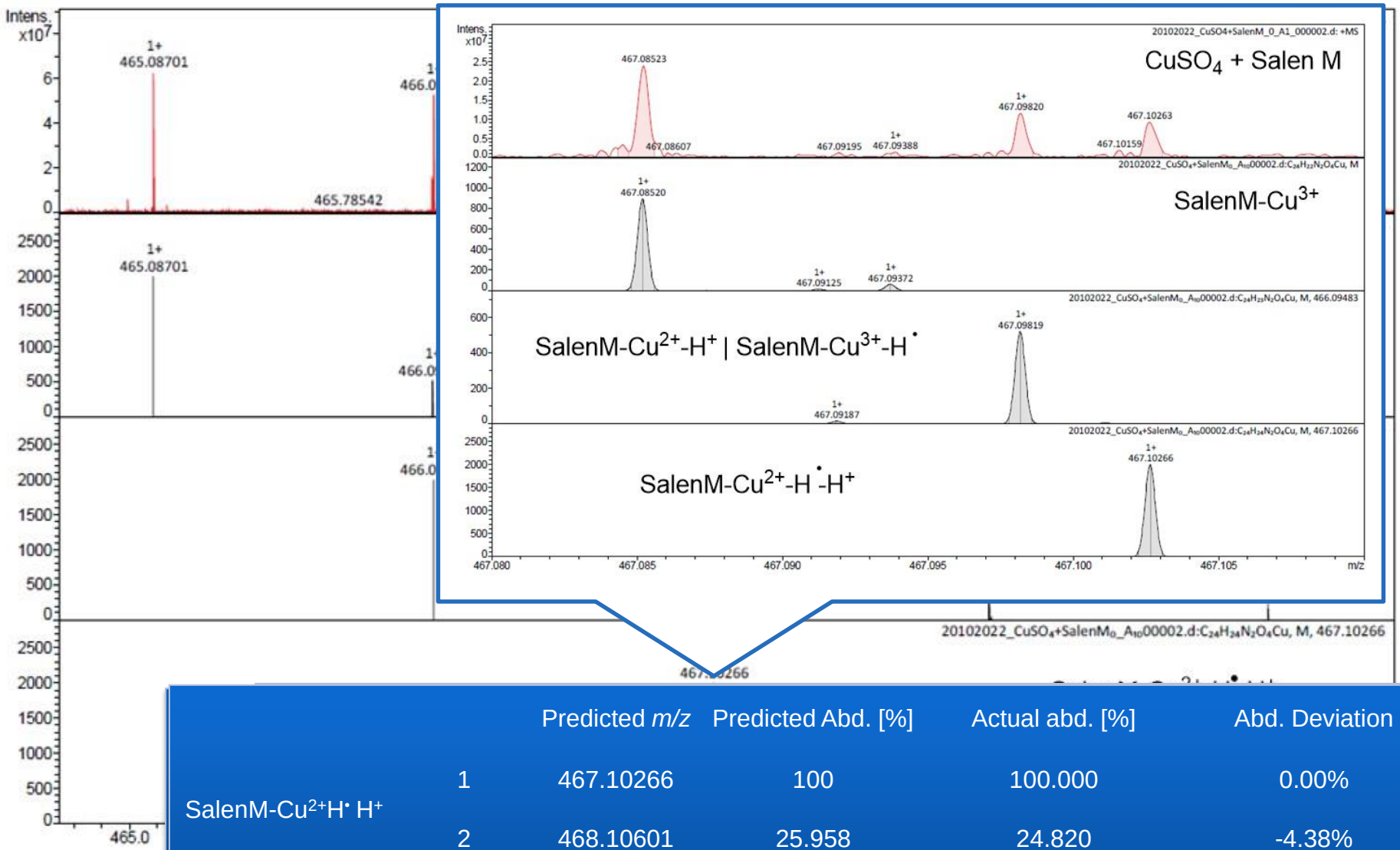
Methanol



N,N'-bis(methoxy-salicylidene)-4,5-methyl-1,2-phenylediamine



Detection of copper salt with synthesized Salen (Salen M)

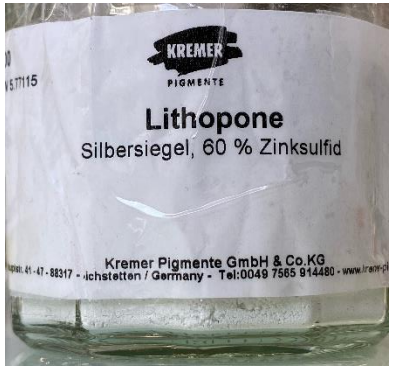


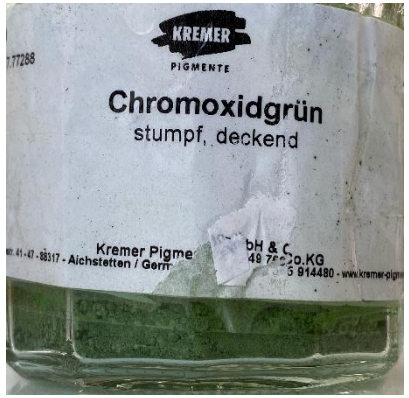
$$ratio = \frac{Total\ intensities\ per\ speciation}{Sum\ of\ total\ intensities\ of\ all\ speciations}$$

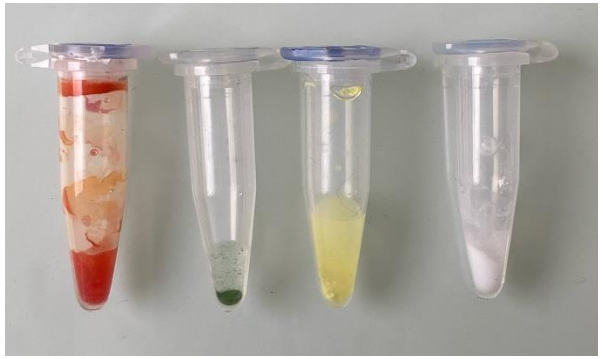
		Predicted *m/z*	Predicted Abd. [%]	Actual abd. [%]	Abd. Deviation	*m/z* deviation (ppm)	Ratio [%]
SalenM-$Cu^{2+}H^{\bullet}$ H^{+}	1	467.10266	100	100.000	0.00%	-0.056	
	2	468.10601	25.958	24.820	-4.38%	0.276	7.4
	3	469.10085	44.613	47.735	7.00%	-0.017	

Dissolution of pigments

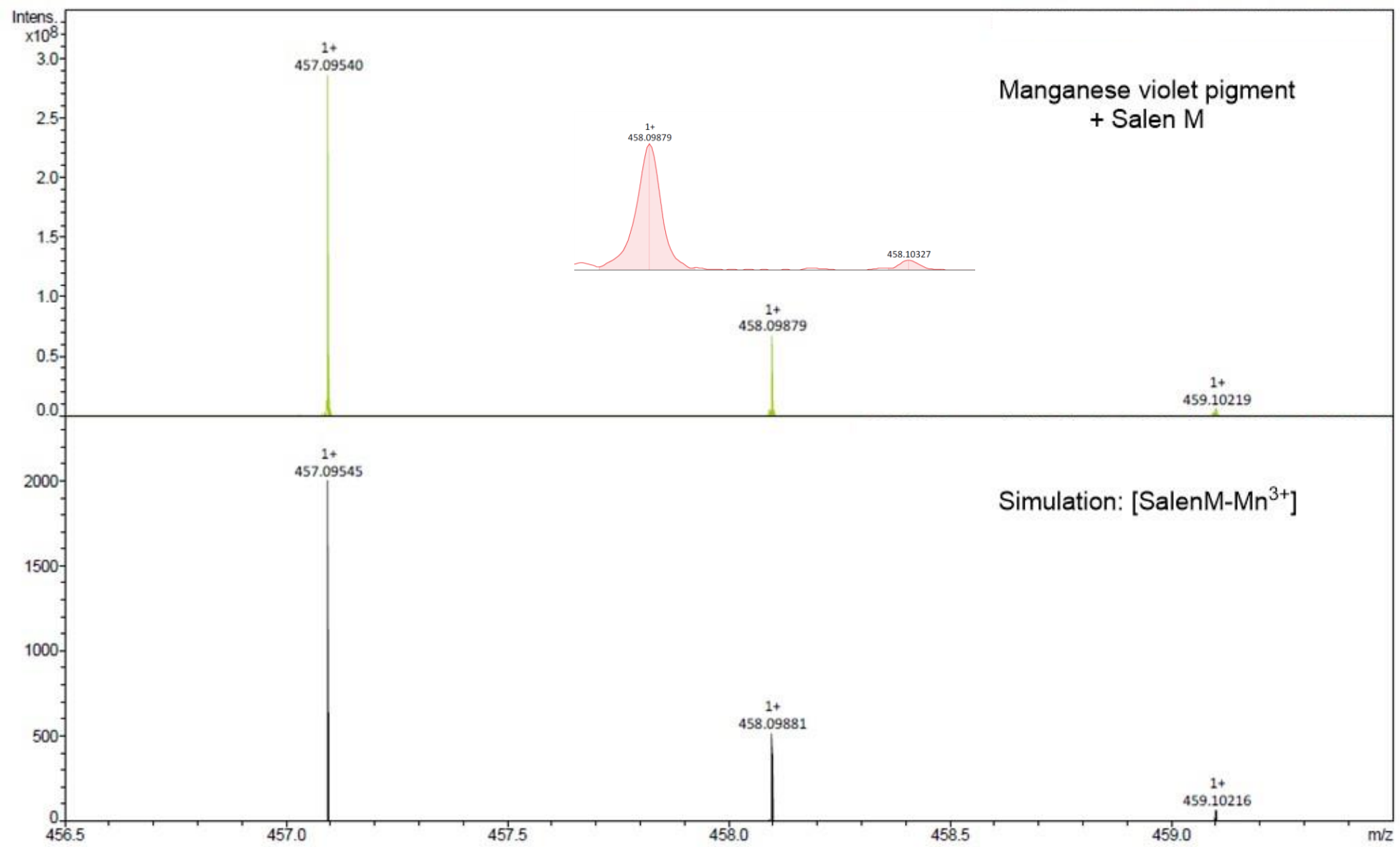
Pigment No	Pigment name	Composition	Dissolution in HF	Complexation with Salen M
PBk11	Black iron oxide	Fe_3O_4	Yes	Yes
PV16	Manganese violet	$NH_4MnP_2O_7$	Yes	Yes
PB35	Cobalt light blue	$CoO.SnO_2$	Yes	Yes
PB28	Cobalt medium blue	$CoAl_2O_4$	Yes	Yes
PB36	Cobalt turquoise dark blue	$Co(Cr.Al)_2O_4$	No	No
PB36	Cobalt greenish blue	Co-Cr-Al-Oxide-Spinel	No	No
PW7	Lithopone	ZnS	No	No
PR102	Venetian italian	$FeO(OH)$, Fe_2O_3	Yes	Yes
PBr7	Raw sienna	Fe_2O_3, Al_2O_3, MnO_2	Yes	Yes
PR108	Cadmium red	CdSe	No	No
PG17	Chromium oxide	Cr_2O_3	No	No
PY53	Nickel titane yellow	$(Ti,Ni,Sb)O_2$	No	No
PR106	Natural cinnabar	HgS	No	No
PR233	Old pink	$Ca(Sn,Cr)SiO_5$	Yes	No





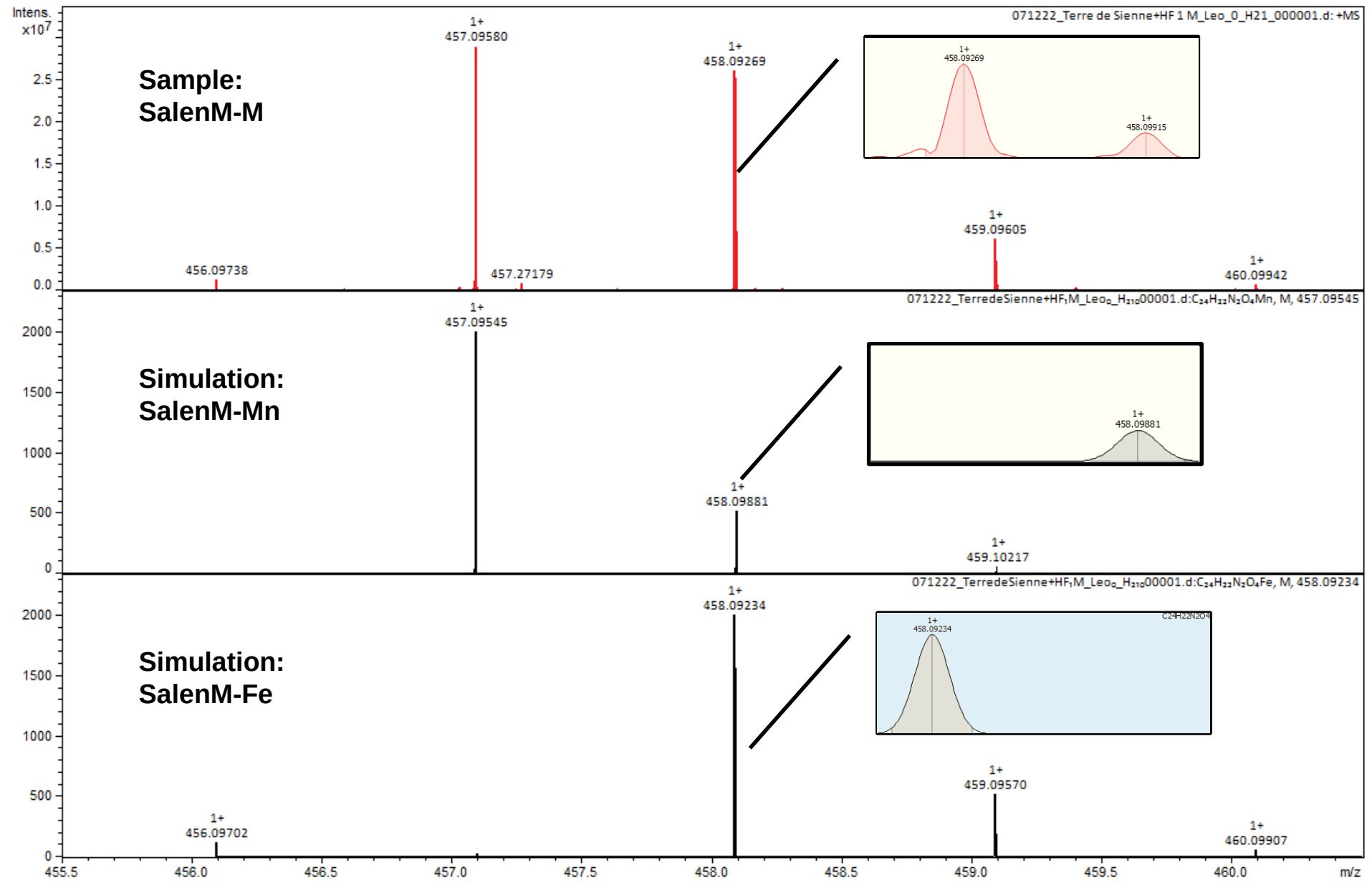


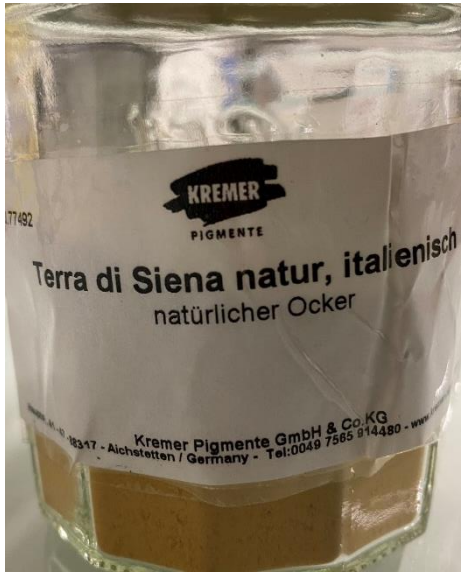
Dissolution of pigments



10 mg/mL of pigment
in 1 M HF

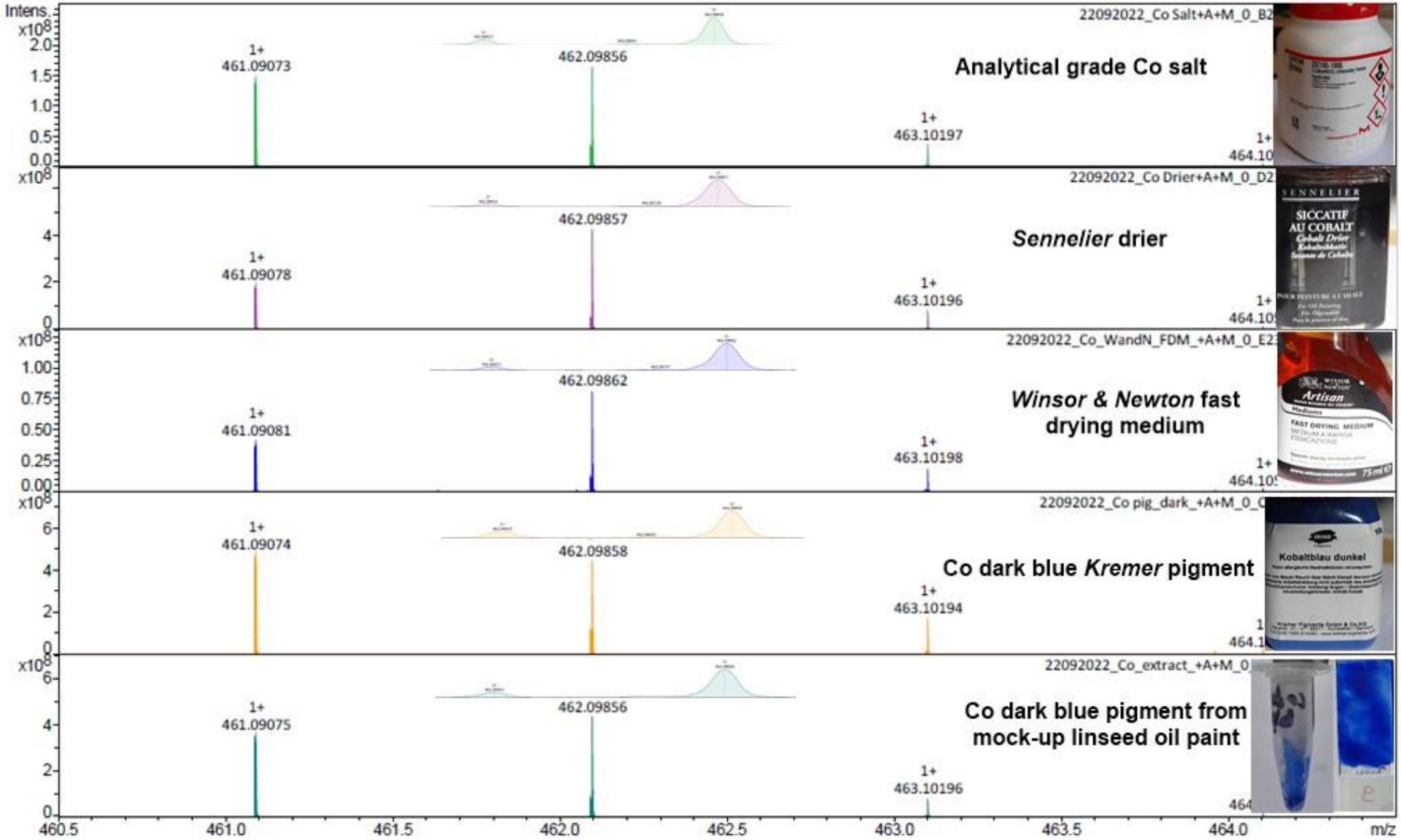
Identification in earth pigments

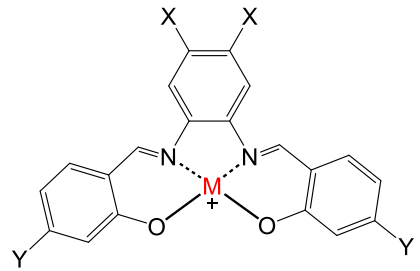




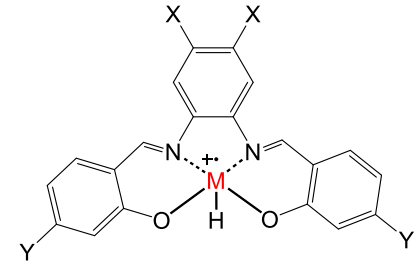
- $Fe_2O_3 \cdot nH_2O$
- $Al_2O_3 \cdot MnO_2$
- $SiO_2 \cdot H_2O$

Results on driers and mock-up linseed oil paints

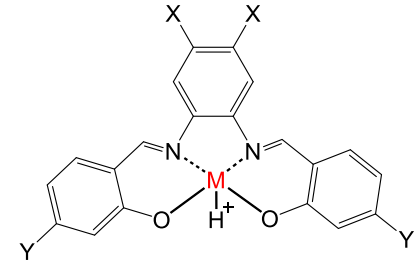




Oxidized speciation
[Salen-M^{3+}]

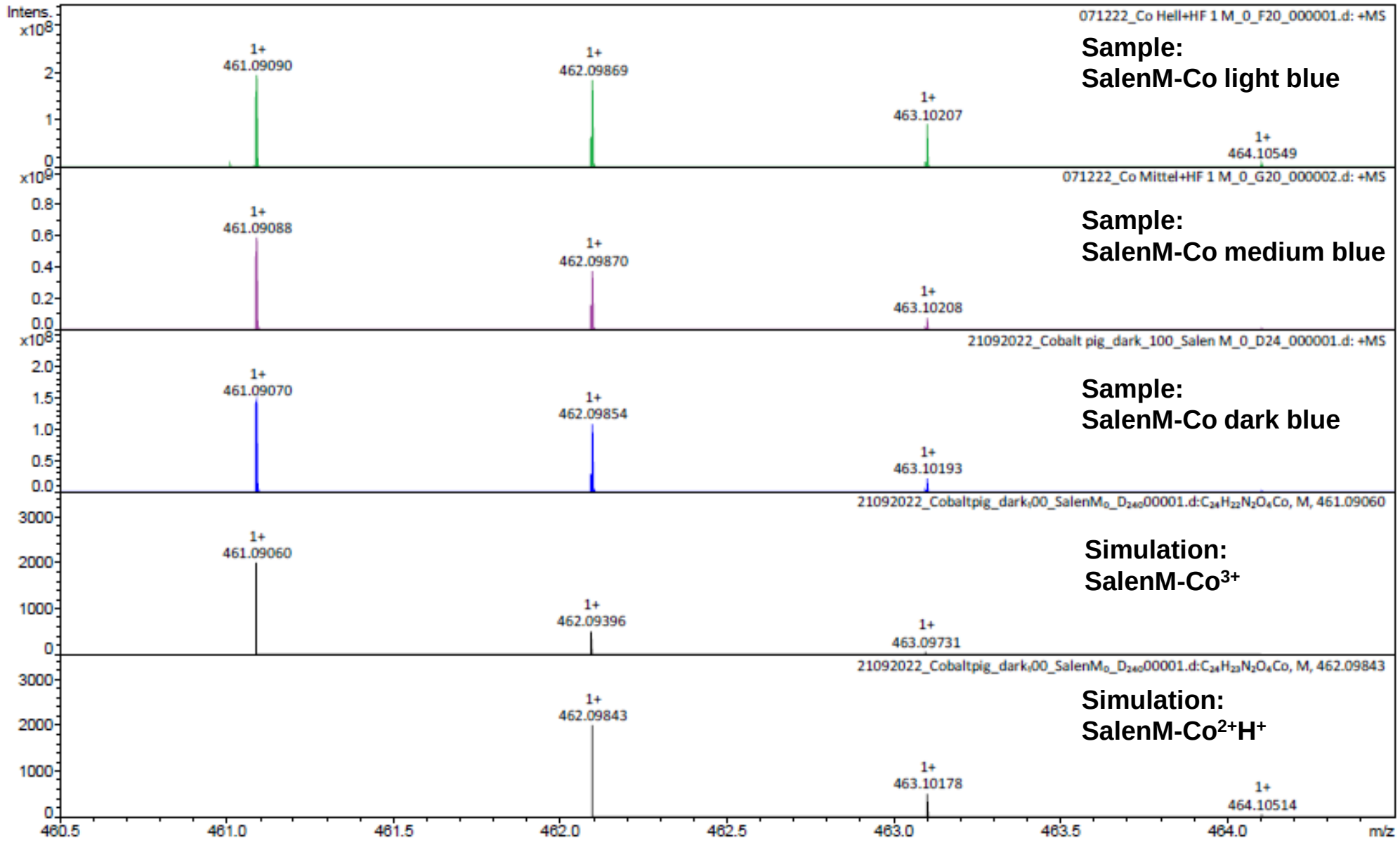


Radical speciation
[Salen-$M^{3+}H^{\bullet}$]



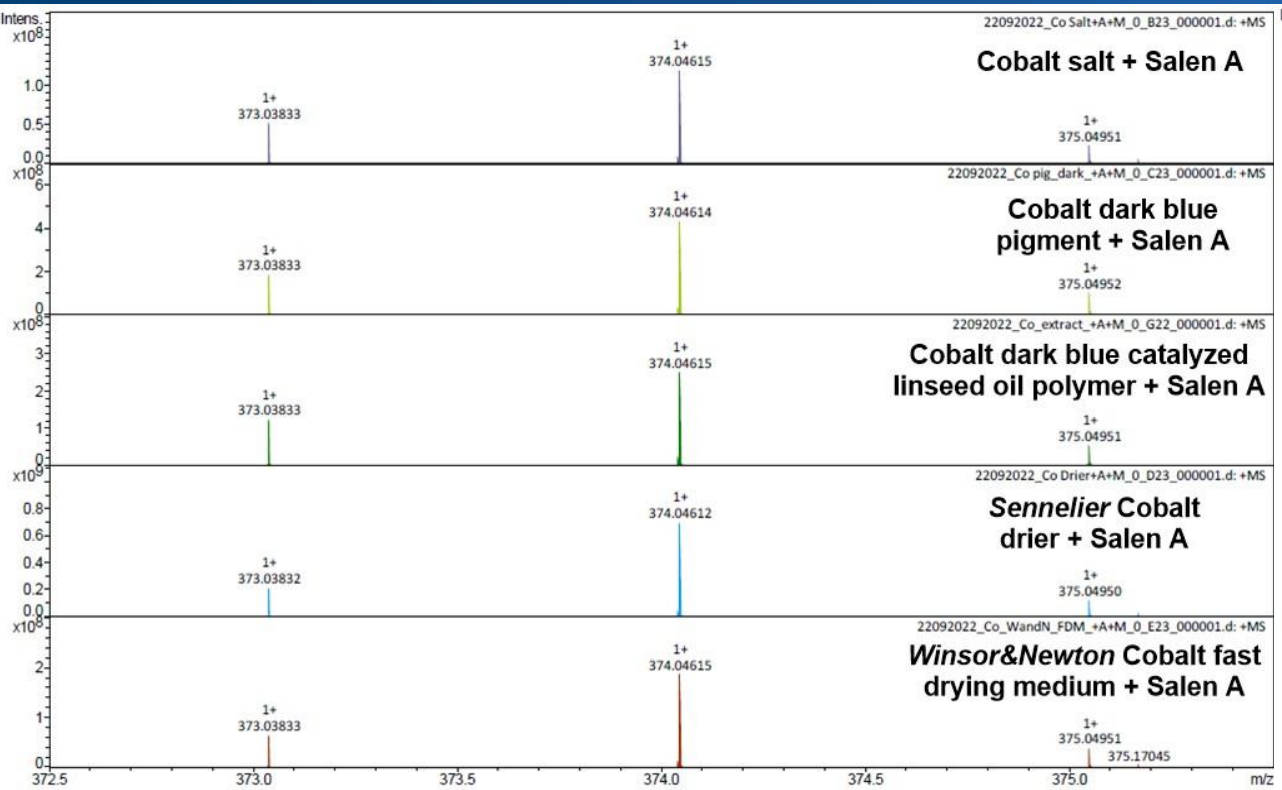
Protonated speciation
[Salen-$M^{2+}H^{+}$]

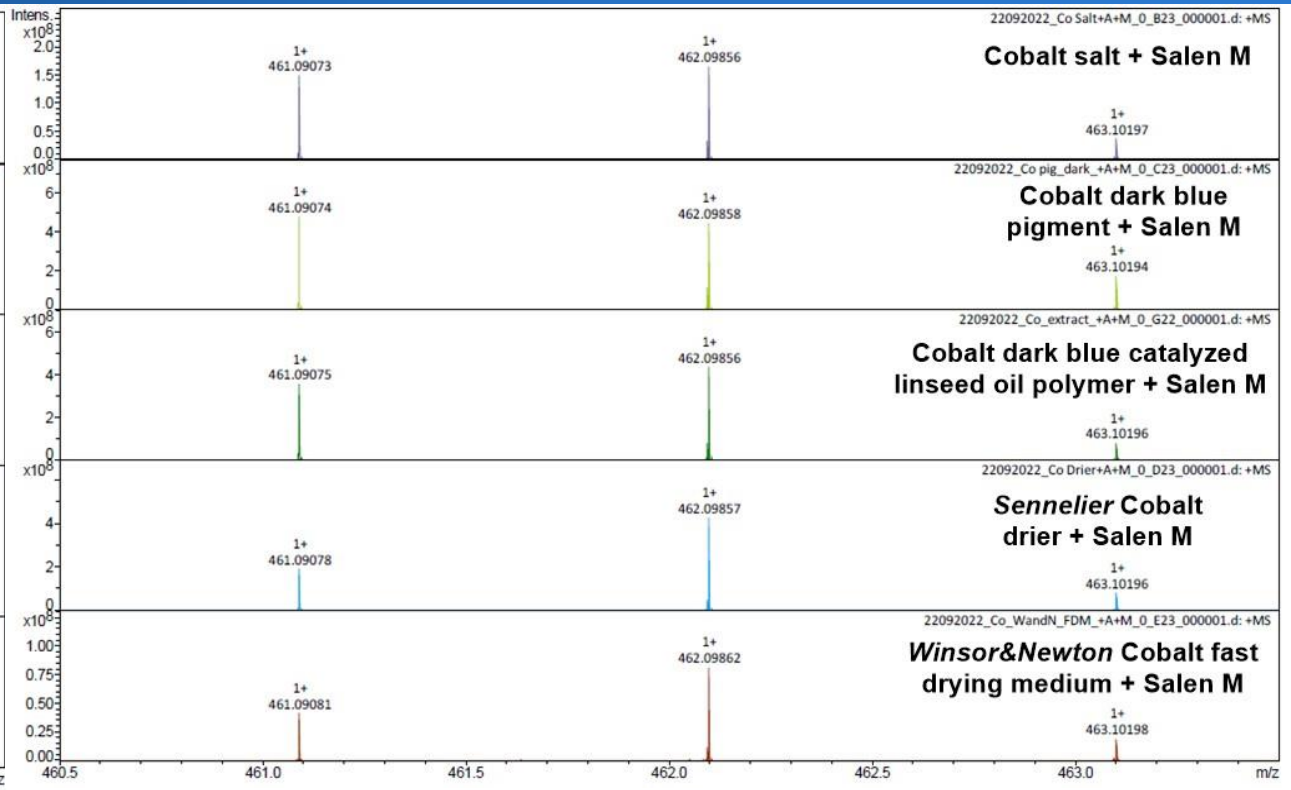
Comparison between different Cobalt pigments



Cobalt light blue	26,16%
Cobalt medium blue	58,90%
Cobalt dark blue	14,94%

Competition between Salen A and Salen M





	Salen A	*m/z*	I	Relative abd.	Salen M	*m/z*	I	Relative abd.
Cobalt drier	[SalenA-M^{3+}]	373.0383	2.17E+08	20.8%	[SalenM-M^{3+}]	461.0907	1.92E+08	27.3%
	SalenA-$M^{3+}H^{\bullet}$ / SalenA-$M^{2+}H^{+}$	374.0461	7.01E+08	67.4%	SalenM-$M^{3+}H^{\bullet}$ / SalenM-$M^{2+}H^{+}$	462.0985	4.27E+08	60.8%
	SalenA-$M^{2+}H^{\bullet}$ H^{+}	375.0495	1.22E+08	11.8%	SalenM-$M^{2+}H^{\bullet}$ H^{+}	463.1019	8.42E+07	12.0%
			1.04E+09				7.03E+08	
						SalenM/SalenA=	**0.68**	
Cobalt salt	[SalenA-M^{3+}]	373.0383	5.25E+07	27.0%	[SalenM-M^{3+}]	461.0907	1.50E+08	42.4%
	SalenA-$M^{3+}H^{\bullet}$ / SalenA-$M^{2+}H^{+}$	374.0461	1.18E+08	60.8%	SalenM-$M^{3+}H^{\bullet}$ / SalenM-$M^{2+}H^{+}$	462.0985	1.66E+08	46.9%
	SalenA-$M^{2+}H^{\bullet}$ H^{+}	375.0495	2.38E+07	12.2%	SalenM-$M^{2+}H^{\bullet}$ H^{+}	463.1019	3.79E+07	10.7%
			1.95E+08				3.53E+08	
						SalenM/SalenA=	**1.82**	

Conclusions and Perspectives

- FT-ICR mass spectrometry proved to be a powerful tool thanks to its high resolution that allows to distinguish between different species.
- MALDI MS analysis consumes only 0.1 µg of metal therefore it is applicable to museum size samples allowing a simultaneous analysis of the pigments and organic binder.
- The present study paves the way for future research on determining the origin of pigments by measuring metal isotope ratios and other trace metal contaminants.

Acknowledgements

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