Electronic Supplementary Material (ESI) for Analytical Methods.

Lead electroanalysis in paints for high impact control in homes

Electronic Supplementary Information (ESI)

Andrés Ansín,[a] Giovanni Galietta,[b] Santiago Botasini[a] and Eduardo Méndez.*[a]

[a] Laboratorio de Biomateriales, Instituto de Química Biológica, Facultad de Ciencias, Universidad de la República. Iguá 4225, 11400 Montevideo, Uruguay.

[b] Unidad de Tecnología de Alimentos. Facultad de Agronomía, Universidad de la República. 12900 Montevideo, Uruguay.

S1. World status on legally binding controls on lead paint

The following text is from “Update on the global status of legal limits on lead in paint, September 2018”, United Nations Environment Programme (2018):

As of 30 September 2018, 71 countries have legally binding controls to limit the production, import and sale of lead paints, which is 36.8% of all countries.

As of 30 September, 2018, 71 countries had confirmed that they have legally binding controls on lead in paint, 78 stated that they do not, and information was unavailable for the remaining 44 countries

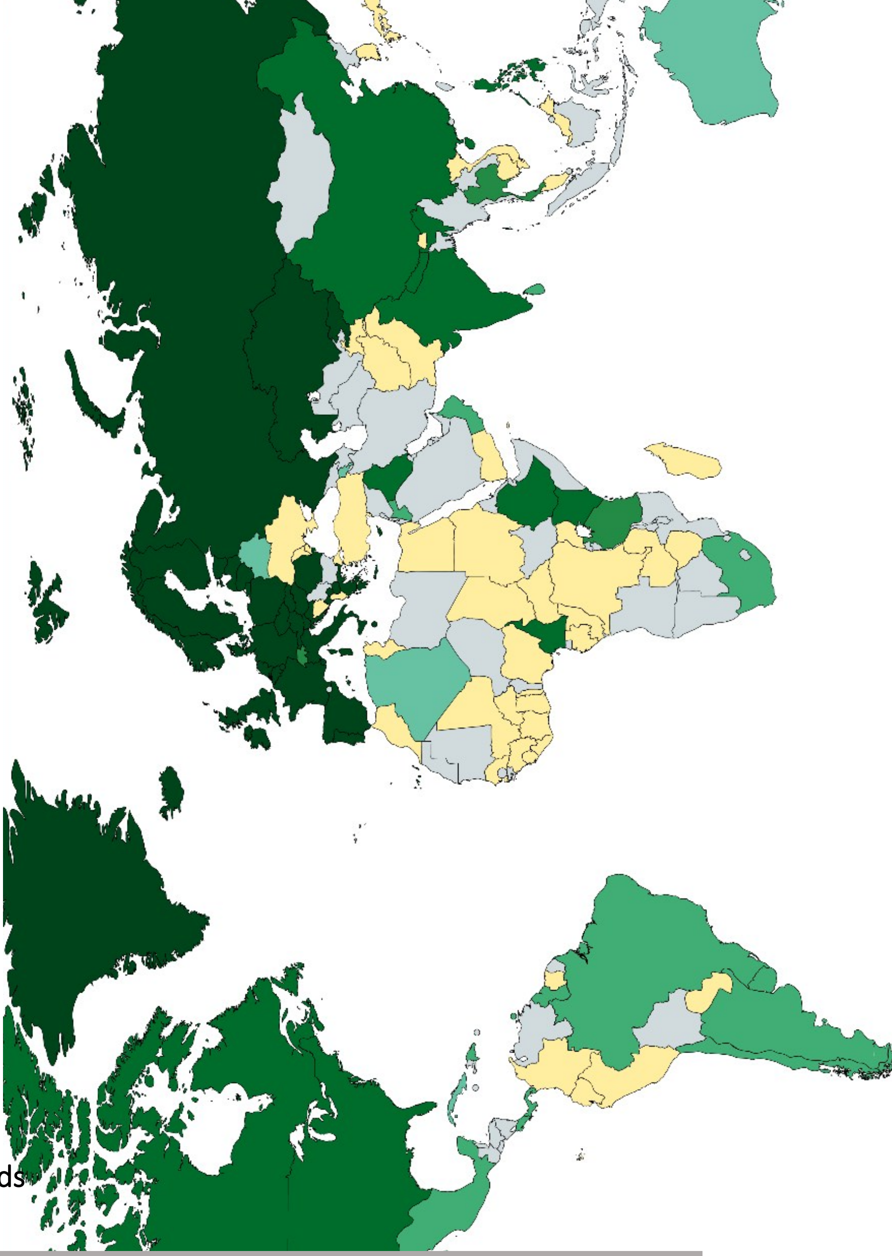
Countries that have enacted laws to limit the lead content in paint have generally used one of two approaches:

(1) establish a single regulatory limit on the total concentration of lead in paint from all sources (currently used in 31 countries) or

(2) establish a set of chemical-specific regulatory limits based on the management of risks of individual lead compounds that are used as additives in paint (currently used in the EU's Registration, Evaluation, Authorisation and Restriction of Chemical (REACH) regulation).

Legal Approach 1: Regulatory Limits on Total Lead Concentration
Of the 71 countries with lead paint laws, 33 countries have established a single regulatory limit on the total or soluble lead concentration in paint (in parts per million). These existing lead limits range from 90 ppm to 1,000 ppm or higher. Twenty-seven countries have a limit of 90, 100 or 600 ppm, which are all relatively low levels and indicate that lead compounds have probably not been added to the paint. Among countries with low limits, only one country uses a regulatory limit on soluble lead content, which is somewhat less protective than a limit on total lead content. There may be additional countries that also currently use a regulatory limit on soluble rather than total lead.

Legal Approach 2: Chemical-Specific Regulatory Limits
Chemical-specific regulatory limits are used by 38 countries, of which 31 have adopted the EU REACH regulation on lead compounds in paints. EU REACH restricts the addition of certain specific lead compounds to paints intended for supply to the general public, based on risk management assessments. Some specific lead compounds for use in paints are subject to an authorization procedure for manufacturers and importers that requires analyses of health and environmental risks and the availability of non-lead alternatives.



S2. Solubility of some lead compounds

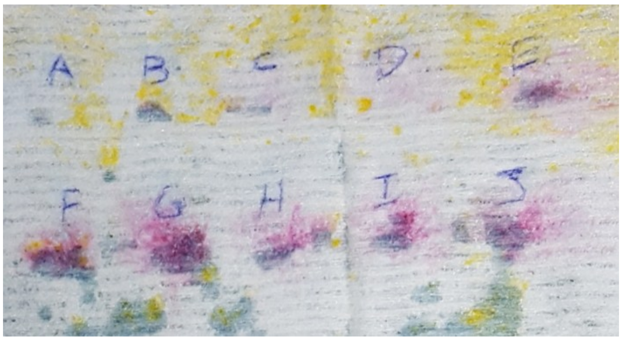
Lead compound	Formula	Molar mass (g/mol)	Solubility in water (g/L)	Solubility in acid and base
Lead carbonate	$PbCO_3$	267.2	insoluble	Acids and bases
Lead chromate	$PbCrO_4$	323.2	insoluble	HNO_3 dil. and bases
Lead hydroxyde	$Pb(OH)_2$	241.2	0.016	Acids and bases
Lead (II) oxide	PbO	223.2	0.0017	HNO_3
Lead (IV) oxide	PbO_2	239.2	insoluble	HCl, HNO_3 dil + H_2O_2, $H_2C_2O_4$
Lead phosphate	$Pb_3(PO_4)_2$	811.5	insoluble	HNO_3 and bases
Lead sulphate	$PbSO_4$	303.3	0.00425	NaOH
Lead sulphide	PbS	293.3	0.0006	Hot HCl dil

S3. Implementation of the Dust Wipe Method (DWM)

The limit of detection (LOD) for the Dust Wipe Method described in NIOSH Method #9105 is between 5 – 10 µg. According to Feigel, the LOD for the drop spot test is between 5 – 15 µg. Known interferences for this test are Tl(I), Ag(I), Cd(II), Ba(II) and Sn(II), which also form coloured compounds with the rhodizonate ion, but with less sensitivity than Pb(II). Also, Pb(II) is the only ion that gives the characteristic pink or red colour.

As other components present in the wipe medium (e.g. surfactants) could interfere, the limit of detection was checked with the commercial wet wipes employed.

Wet wipes used are originally commercialised for toilette paper (left) or for baby cleaning (right). Pictures taken by E. Méndez.



Amount of Pb in each spot (in µg): A = 1, B = 2, C = 5, D = 7, E = 10, F = 20, G = 40, H = 60, I = 80, and J = 100. Picture taken by A. Ansín.

The assay was carried out by triplicate, by addition of the same volume of Pb(II) containing solutions in the range 1 - 100 µg. The spot with the lower Pb concentration giving clearly positive is considered as “positive”. In the Figure, it corresponds to spot “E”, with 10 µg. Notice that C and D still gave a positive output, but could not be conclusive in on-site operations. In these cases, these results are considered “suspicious”.

The size of the spots are *ca*. 10 cm^2, meaning that the LOD is *ca*. 1 µg/cm^2 for a positive result, and 0.5 µg/cm^2 for a suspicious result.

How these values relate to the Pb content in the paint is still a matter of controversy, but as a reference, the limits established in some norms indicate that the Pb content in paints should not exceed 0.1 mg/cm^2 or 600 mg/kg. If the proportion continues, the equivalence would be 90 mg/kg to 15 µg/cm^2. Hence, the DWM is adequate as a screening on-site method for Pb in paints.

References

Feigel, A.V. Spot Tests in Inorganic Analysis. (1972). Elsevier (Amsterdam), pp. 282-287, 564-566, 569

S4. Derivation of equation (1)

The complete protocol for the determination of the Pb content in paint chips involve the following steps:

Step	**Procedure**	**Parameter involved (units)**	**Value or Range**	**Can be varied?**
1.	Weight a sample of paint chips	m_{sample} (g)	0.050 – 0.400	YES, in the range specified by the NIOSH Method 7701
2.	Digestion to a final volume	$V_{\text{digestion}}$ (mL)	50	NO. Official technique NIOSH Method 7701.
3.	Take an aliquote of the digestion	V_{aliquote} (µL)	100 - 500	YES, in a limited range, while the Pb normalized currente is within the 0 – 100 µg/L range.
4.	Dilute sample 1/*f* (*f* = dilution factor) for high Pb content	f	as needed	YES, in ordert that the Pb normalized current is within the 0 – 100 µg/L range.
5.	Add buffer to the electrochemical cell to a final volume	V_{cell} (mL)	10	NO, is the final volume for which the present electrochemical technique was validated.

Let's consider a sample with a Pb content of "$\text{Pb}_{\text{sample}}$" (mg Pb/kg sample). The Pb content in each step summarized in the Table above are:

Step 1.

$$Pb\ (in\ mg) = \frac{Pb_{sample}\, m_{sample}}{1000}$$

Step 2.

$$Pb\ (inmg/mL) = \frac{Pb_{sample}\, m_{sample}}{1000\, V_{digestion}}$$

Step 3.

$$Pb\ (in\ mg) = \frac{Pb_{sample}\, m_{sample}\ V_{aliquote}}{(1000)^2\, V_{digestion}}$$

Step 4.

$$Pb\ (in\ mg) = \frac{Pb_{sample}\, m_{sample}\ V_{aliquote}}{(1000)^2\, V_{digestion}\, f}$$

Step 5.

$$Pb_{solution}\ (in\ \mu g/L) = \frac{Pb_{sample}\, m_{sample}\ V_{aliquote}}{V_{digestion}\, f\, V_{cell}}$$

In this equation, V_{cell} = 10 mL and $V_{\text{digestion}}$ = 50 mL cannot be changed. Hence, the equation for the calculation of $\text{Pb}_{\text{sample}}$ (in mg/kg) is:

$$Pb_{\ sample}(mg/kg) = \frac{500\ (mL^2)\ f\ Pb_{solution}\ (\mu g/L)}{m_{sample}(g)\ V_{aliquote}(\mu L)}$$

S5. On-site activities

Most of the measurements were carried out at homes within the neighbourhoods in Montevideo and Canelones (Uruguay). The homes at these neighbourhoods are constructed with basic materials. Inhabitants are not involved in waste recycling as a way of living. In the construction of their homes, old doors and windows, as well as some furniture, are used, mainly obtained as recycled materials from other houses, destroyed for the construction of new ones. Those pieces have been already painted, probably before the ‘80s, constituting one of the main Pb sources in-home. Other Pb source is the use of old paints that are recovered by the addition of suitable solvents.

The following pictures (taken by E. Méndez) illustrate the application of the Dust Wipe Method screening on-site by one of the authors (A. Ansín).

Delimitation of an approximate square of 100 cm^2 for the application of the Dust Wipe Method.

Carry-on kit containing all the elements for the application of the Dust Wipe Method.

Scrapping a paint chip from an old recycled door employed in the construction of a new home.

Kit content for the application of the Dust Wipe Method screening on-site

S6. Analytical calibration plot in the absence of matrix effects

Linear and quadratic fits to the data yield the following parameters:

	Value	Standard error	t-value	P > |t|	95 % confidence range
Linear fit					
Intercept	-0.00577	0.00139	-4.14075	3.45x10^{-4}	(-0.00863) – (-0.0029)
Slope	6.61x10^{-4}	0.28x10^{-4}	23.9888		(6.04x10^{-4}) – (7.18x10^{-4})
Quadratic fit					
Intercept	-0.00103	0.00181	-0.57208	0.57259	(-0.00477) – (0.0027)
Linear term	3.32x10^{-4}	0.99x10^{-4}	3.35952	0.0026	(1.28x10^{-4}) – (5.36x10^{-4})
Quadratic term	3.23x10^{-6}	0.94x10^{-6}	3.4218	0.00223	(1.28x10^{-6}) – (5.18x10^{-6})

For the linear fit, Student's test statistic reject the null hypothesis (intercept = 0) and hence, at 95 % confidence limit, the fitted intercept is significantly different from zero. Also, the confidence limit interval for the intercept does not include the zero value, reinforcing the idea of a non-zero intercept. In the case of the quadratic fit, Student's test statistic accept the null hypothesis, and therefore, at the 95 % confidence limit the intercept is NOT significantly different from zero.

These results suggest that the quadratic model should give a better fit to the data than the linear model. The ANOVA-LOF test, however, do not give significant evidence of lack of fit for both models at 95 % confidence limit.

	DF	Sum of squares	Mean square	F value	Prob>F
Linear fit					
Lack of fit	7	1.866x10^{-4}	2.666x10^{-5}	1.47883	0.23663
Pure error	18	3.2447x10^{-4}	1.803x10^{-5}		
Error	25	5.11x10^{-4}			
Quadratic fit					
Lack of fit	6	1.902x10^{-5}	3.171x10^{-6}	0.1759	0.97996
Pure error	18	3.245x10^{-4}	1.803x10^{-5}		
Error	24	3.435x10^{-4}			

In view of these results, both models were compared, using different criteria, namely, Akaike's Information Criterion Test (AIC), Bayesian Information Criterion Test (BIC), and Mandel's test (F-test).

AIC Test

	RSS	N	Params	AIC	Akaike Weight
Linear model	5.1107×10^{-4}	27	2	-286.57748	0.0184
Quadratic model	3.4349×10^{-4}	27	3	-294.53097	0.9816

BIC Test

	RSS	N	Params	BIC	Diff BIC
Linear model	5.1107×10^{-4}	27	2	-283.73345	7.43235
Quadratic model	3.4349×10^{-4}	27	3	-291.1658	0

F-test

F	Numer.DF	Denom.DF	Prob > F
11.70869	1	24	0.00223

At 95 % confidence level, the 3 tests indicate that the quadratic model is more likely to be correct than the linear model.

S7. Analytical calibration plot in the presence of Pb-free CRM (assessment of matrix effects)

Linear and quadratic fits to the data yield the following parameters:

	Value	Standard error	t-value	P > |t|	95 % confidence range
Linear fit					
Intercept	-0.00479	7.88×10^{-4}	-6.08121	2.35×10^{-6}	(-0.00641) – (-0.00317)
Slope	5.86×10^{-4}	0.16×10^{-4}	37.61669		(5.54×10^{-4}) – (6.18×10^{-4})
Quadratic fit					
Intercept	-8.38×10^{-4}	6.66×10^{-4}	-1.25797	0.2205	(-0.00221) – (5.37×10^{-4})
Linear term	3.12×10^{-4}	0.36×10^{-4}	8.55652	9.4×10^{-9}	(2.36×10^{-4}) – (3.87×10^{-4})
Quadratic term	2.70×10^{-6}	0.35×10^{-6}	7.75851	5.4×10^{-8}	(1.98×10^{-6}) – (3.41×10^{-6})

For the linear fit, Student's test statistic reject the null hypothesis (intercept = 0) and hence, at 95 % confidence limit, the fitted intercept is significantly different from zero. Also, the confidence limit interval for the intercept does not include the zero value, reinforcing the idea of a non-zero intercept. In the case of the quadratic fit, Student's test statistic accept the null hypothesis, and therefore, at the 95 % confidence limit the intercept is NOT significantly different from zero.

These results suggest that the quadratic model should give a better fit to the data that the linear model. The ANOVA-LOF test, indicate that only the quadratic model do not give significant evidence of lack of fit at 95 % confidence limit. Hence, according to this criterion, the linear model can be disregarded.

	DF	Sum of squares	Mean square	F value	Prob>F
Linear fit					
Lack of fit	7	1.2496×10^{-4}	1.785×10^{-5}	8.3361	1.408×10^{-4}
Pure error	18	3.8546×10^{-5}	2.1414×10^{-6}		
Error	25	1.635×10^{-4}			
Quadratic fit					
Lack of fit	6	8.0618×10^{-6}	1.3436×10^{-6}	0.62744	0.70647
Pure error	18	3.8546×10^{-5}	2.1414×10^{-6}		
Error	24	4.6608×10^{-5}			

Additional support was obtained using the other criteria: Akaike's Information Criterion Test (AIC), Bayesian Information Criterion Test (BIC), and Mandel's test (F-test).

AIC Test

	RSS	N	Params	AIC	Akaike Weight
Linear model	1.63504×10^{-4}	27	2	-317.34822	1.754×10^{-7}
Quadratic model	4.66076×10^{-5}	27	3	-348.46058	1

BIC Test

	RSS	N	Params	BIC	Diff BIC
Linear model	1.63504×10^{-4}	27	2	-314.5402	30.59122
Quadratic model	4.66076×10^{-5}	27	3	-345.0954	0

F-test

F	Numer.DF	Denom.DF	Prob > F
60.19454	1	24	5.406×10^{-8}

At 95 % confidence level, the three tests indicate that the quadratic model is more likely to be correct than the linear model.

S8. Analytical calibration plot in the presence of Pb-CRM (recovery assay)

The inverse addition standard method was employed in order to obttain the recovery directly from the Y-axe. Linear and quadratic fits to the data yield the following parameters:

	Value	Standard error	t-value	P > |t|	95 % confidence range
Linear fit					
Intercept	-43.47491	3.14187	-13.83726	8.16986 x 10^{-4}	(-53.47376) – (-33.47606)
Slope	1190.83467	35.55057	33.49692	5.84877 x 10^{-5}	(1077.69679) – (1303.97255)
Quadratic fit					
Intercept	-53.413	6.63174	-8.05415	0.01507	(-81.94706) – (-24.87893)
Linear term	1480.34446	180.86437	8.18483	0.0146	(702.14787) – (2258.54105)
Quadratic term	1480.34446	1125.08105	-1.62113	0.24644	(-6664.73545) – (3016.93068)

The ANOVA-LOF test, indicate that the quadratic model do not give significant evidence of lack of fit at 95 % confidence limit. Hence, according to this criterion, the linear model can be disregarded.

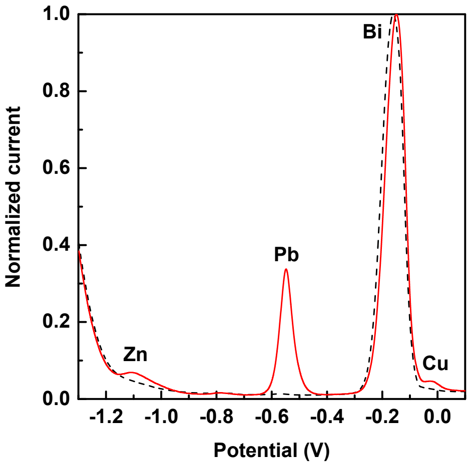
	DF	Sum of squares	Mean square	F value	Prob>F
Linear fit					
Lack of fit	1	5904.21395	5904.21395	1122.04379	5.84877x10^{-5}
Pure error	3	15.78605	5.2620		
Error	4	5920			
Quadratic fit					
Lack of fit	2	5913.17812	2956.58906	866.79535	0.00115
Pure error	2	6.82188	3.41094		
Error	4	5920			

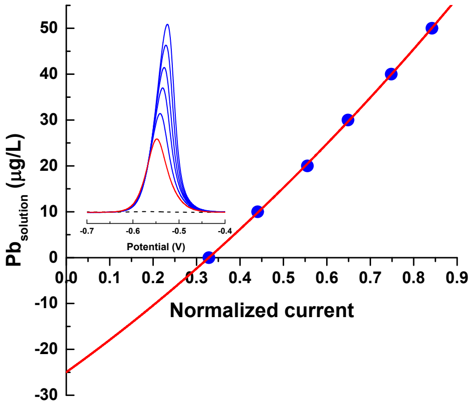
The quadratic model is chosen for this analysis, and as a consequence, the $Pb_{solution}$ concentration is 53.4 ± 6.6 µg/L.

S9. SWASV and FTIR analyses of paint chip samples

S9.1. Details of Case I

The electrochemical analysis (dilution 1/10) shows the presence of Pb, along with Zn and Cu.

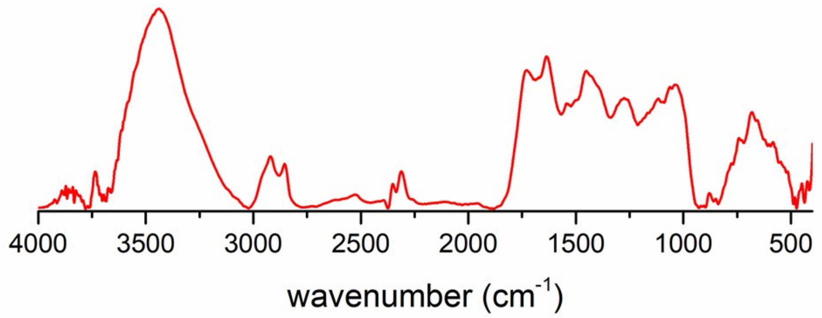




The standard addition method yielded a quadratic curve that represents a better fit than the straight line (BIC and F-Test criteria, AIC criterium favours the straight line curve). The axes were interchanged in order to obtain the $Pb_{solution}$ directly from the graph, as well as the 95 % confidence interval.

$Pb_{solution}$ = 25 µg/L
(19 µg/L – 30 µg/L, 95 % confidence interval)
Pb_{sample} = 30,000 mg/kg
(23,000 mg/kg – 36,000 mg/kg, 95 % confidence interval)

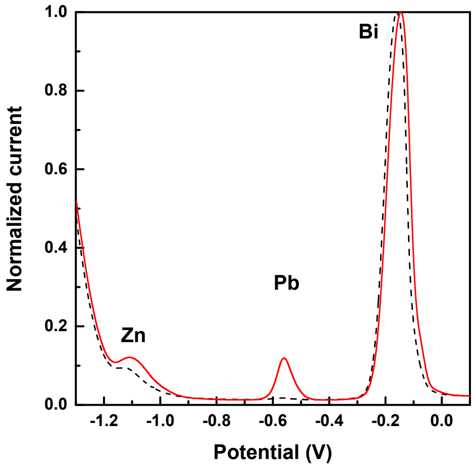
FTIR analysis confirm the presence of chrome yellow ($PbCrO_4$) as pigment, and linseed oil as binder.

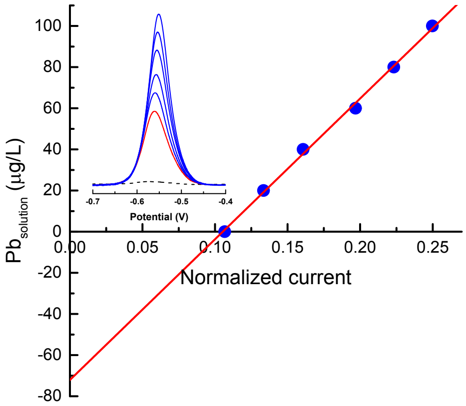


Crome yellow (cm^{-1})	**Linseed oil (cm^{-1})**	**Experimental (cm^{-1})**	**Assignation**
	459 *w*	448 *w*	Linseed oil
595 *s*	581 *m*	580 *sh*	Linseed oil
627 *s*		649 *s*	$PbCrO_4$
		677 s	?
	721 *s*	730 *w*	Linseed oil
853 *s*		848 *w*	$PbCrO_4$
967 *w*			
1040 *s*		1033 *s*	$PbCrO_4$
	1098 *m*		
1173 *sh*	1160 *s*	1121 *s*	$PbCrO_4$ + Linseed oil
	1237 *m*		
		1270 *s*	?
	1461 *m*	1453 *s*	Linseed oil
	1655 *w*	1634 *s*	Linseed oil
	1742 *s*	1733 *s*	Linseed oil
	2853 *s*	2853 *m*	Linseed oil
	2923 *s*	2922 *m*	Linseed oil
	3010 *m*		
		3440 *s*	

S9.2. Details of Case II

The electrochemical analysis (1/100 dilution) confirms the presence of Pb as well as Zn.

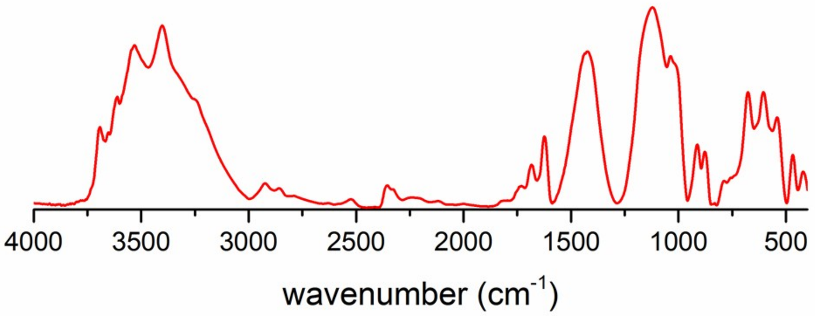




The standard addition method yielded a straight line that represents a better fit than the quadratic curve (supported by AIC and F-Test criteria, while BIC criteria was not conclusive). The axes were interchanged in order to obtain the Pb$_{solution}$ directly from the graph, as well as the 95 % confidence interval.

Pb$_{solution}$ = 72 µg/L
(64 µg/L – 80 µg/L, 95 % confidence interval)
Pb$_{sample}$ = 90,000 mg/kg
(80,000 mg/kg – 100,000 mg/kg, 95 % confidence interval)

FTIR analysis confirm the presence of lead white ($2PbCO_3{\cdot}Pb(OH)_2$) as pigment, and gypsum ($CaSO_4.2H_2O$) as filler.



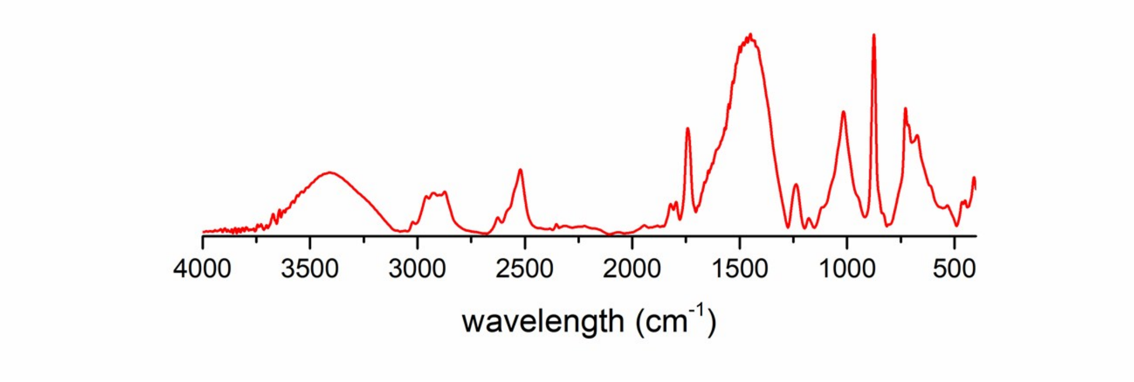
Lead white (cm^{-1})	**Gypsum (cm^{-1})**	**Experimental (cm^{-1})**	**Assignation**
	418 *m*	418 *m*	$CaSO_4.2H_2O$
	460 *m*	468 *m*	$CaSO_4.2H_2O$
		541 *m*	?
	596 *s*	604 *s*	$CaSO_4.2H_2O$
	667 *s*		
678 *s*		676 *s*	$2PbCO_3\cdot Pb(OH)_2$
691 *sh*			
	729 *w*		
762 *m*			
833 *w*			
853 *w*			
	879 *m*	876 *m*	$CaSO_4.2H_2O$
891 *w*			
	1005 *sh*	1003 *m*	$CaSO_4.2H_2O$
1045 *s*		1035 *s*	$2PbCO_3\cdot Pb(OH)_2$
	1108 *s*	1121 *s*	$CaSO_4.2H_2O$
1364 *sh*			
1397 *s*		1424 *s*	$2PbCO_3\cdot Pb(OH)_2$
	1445 *m*		
1541 *sh*			
	1620 *s*	1623 *m*	$CaSO_4.2H_2O$
	1683 *m*	1683 *m*	$CaSO_4.2H_2O$
1729 *m*		1735 *w*	$2PbCO_3\cdot Pb(OH)_2$
	2324 *w*	2325 *w*	$CaSO_4.2H_2O$
2849 *w*		2858 *w*	$2PbCO_3\cdot Pb(OH)_2$
2916 *w*		2926 *w*	$2PbCO_3\cdot Pb(OH)_2$
	3242 *w*	3244 *sh*	$CaSO_4.2H_2O$
	3402 *s*	3401 *s*	$CaSO_4.2H_2O$
	3526 *s*		
3534 *s*		3534 *s*	$2PbCO_3\cdot Pb(OH)_2$

Relative strength of signals are *w* = weak, *m* = medium, *s* = strong; *sh* = shoulder.

S9.3. Details of Case III

The DWM gave negative results for Pb. The electrochemical analysis gave a minor signal that was processed by the satandard addition method, with axe swapping. The $Pb_{solution}$ extrapolated was 3.6 µg/L < LOD = 14 µg/L. Hence, for the experimental data used in the analysis (m_{sample} = 0.396 g and $V_{aliquot}$ = 500 µL) the lead content in the sample is Pb_{sample} < 35 mg/kg

FTIR analysis show the presence of carbonate salts, no one based on lead, along with linseed oil.



$CaMg(CO_3)_2$ (cm^{-1})	Linseed oil (cm^{-1})	Experimental (cm^{-1})	Assignation
	459 *w*	465 *w*	Linseed oil
	581 *m*		
	721 *s*	720 *s*	Linseed oil
726 *s*		727 *s*	$CaMg(CO_3)_2$
878 *vs*		876 *s*	$CaMg(CO_3)_2$
	1098 *m*	1117 *sh*	Linseed oil
	1160 *s*		
	1237 *m*	1236 *m*	Linseed oil
1431 *vs*	1461 *m*	1450 *s*	$CaMg(CO_3)_2$ + Linseed oil
	1742 *s*	1741 s	Linseed oil
	2853 *s*	2874 *m*	Linseed oil
	2923 *s*	2926 *m*	Linseed oil
	3010 *m*	3021 *w*	Linseed oil
		3406 *s*	

Relative strength of signals are *w* = weak, *m* = medium, *s* = strong; *vs* = very strong; *sh* = shoulder.