

Possibility of direct rapid determination of inorganic contaminant elements in paints by LA-ICP-MS method

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Abstract

In this work content of inorganic major and trace elements were directly determined in produced in China, Russia, and Germany household use purpose oil, acryl, and ochre paint samples using laser ablation-inductively coupled plasma-mass spectroscopy (LA_ICP_MS) technique. A sample preparation was simple and rapid: an oil and acryl paint droplets were dried on glass substrate for several hours on a hot plate at 60° C and few mg ochre paint powder samples were solidified with pure paraffin wax on the glass substrate. Dried oil and acryl paint droplets were ablated locally, drilling the hole way, while ochre paint powders were ablated using surface rastering method.

Contents of inorganic elements were calculated using the NIST 610 glassy standard sample as the reference. Parallel determination results of lead and chromium in oil paint samples by atomic absorption technique correlates with that of by LA_ICP_MS acceptably (correlation coefficient for lead is 0.85 and for chromium is 0.95). Because of sample organic - reference inorganic matrix difference, the measured by the LA_ICP_MS content of each element must be adjusted being multiplied in some quantity, value of which are different for each element. For lead and chromium value of the quantity found correspondingly as 6.4 and 9.3. The average relative standard deviation (RSD) of measured content of the mostly high content elements Ca, Al, Mn, Pb, Sr, S, Mg, Fe, Sb, Na, Co, Si, Zn, Cu, P, Y, K, Cl, Ce, and La is less than 10%, the RSD for elements Ti, Cr, Sn, Ba, Zr, Rb lies between 10 and 20%, and the RSD for trace elements Gd, Nb, Sc, V, U, Pr, Ni, Ga, Eu, As, Th, B, Mo, Cd, Li lies in interval from 20 to 50 %.

High level of concentration 309 – 24300 ppm for lead, 950- 3134 ppm for chromium are detected by LA-ICP-MS method in samples of red, yellow and green color oil paints produced in China and bestselling in Mongolia certain brand products. Up to 1900 ppm alarming high content of arsenic is found in the Chinese origin yellowish red, brown red color ochre paints.

As shows our measurements, the LA-ICP-MS method is possible to use as alternative rapid semi-quantitative detection method with acceptable accuracy and precision for basic inorganic additives in oil, acryl and ochre paints using glassy standard sample.

Keywords Harmful to health elements in paints, LA-ICP-MS method, drill and raster ablation

I. INTRODUCTION

In low income per capita countries like as Mongolia, most of ordinary people buy construction materials for their private house building, home repairing and redesigning work ruling by cheapest price on a market. Cheap construction materials much probably contain dangerous to human health heavy elements like as

lead (Pb), cadmium (Cd), chromium (Cr), arsenic (As), thallium (Tl) and other carcinogenic and toxic elements, organic compounds, creating for people who buy and use these materials a nearly life - long term exposure of the harmful contaminants in their regular residence environment.

In case of Mongolia, vast majority of construction materials available on country's

domestic market are imported ones from China. A less than half of steel carcasses, cements, bricks are produced domestically, but materials for interior-exterior finishing design such as paints, wall papers, floorings, plastics, and ceramics, nearly all of them are imported from China. Products European and Asian brand other than Chinese are also available on the market, but at prices 3-10 times higher than Chinese analogues. For this reason majority of people tends to buy Chinese origin construction- design materials for household use purpose.

In general, quality standard of construction materials regulates by the Mongolian state law [1]. But in practice, because of weak control and shortage of state authority testing laboratory capacity, almost every private seller of construction material is unable to show to buyers any government authority certificate that might confirm quality of selling item. Majority of buyers therefore have been forced to trust only to producer's self-advertisement and self-rating. In these circumstances fast, simple but comprehensive, and relatively cheap elemental analysis method such as LA-ICP-MS (Laser Ablation - Inductively Coupled Plasma - Mass Spectroscopy) [2, 3] method is urgent to develop and implement for auditing of any product, including construction materials in countries such as Mongolia.

The LA-ICP-MS elemental analysis method is widely uses in geochemical trace element analysis of rocks, rock age dating [4, 5], successfully used in archeology [6], forensic analysis [7, 8], soil [9] and marine study [10]. In this method deep UV wavelength, 10-50 ns short laser pulse directly hit a solid sample surface at pulse rates up to 10 Hz. Single pulse energy varies at hundreds of mJ and spatially homogenized in 120 μm diameter focus area. Each pulse vaporizes up to 10 μm thick tiny layer of sample material into fine dust particles which are transported through tubing by flow of argon gas into ICP ionization torch at an analyte ions entrance of a mass spectrometer. Laser ablation direct solid sampling provides many advantages over other sample preparation such as hydride gasification, acid/ base wet digestion, fusing to glass or press pelleting. LA sampling do not need sample milling,

homogenization, digesting in acids, thereby reducing the time and complexity of analysis. Direct LA also may characterized as non-destructive sampling because it takes for analysis few or less milligram amount of sample material and after laser ablation the footprint is the hardly to notice by naked eye microscopic size hole on the surface of the sample. The LA-ICP-MS may also pretend as fastest elemental analytical method. Mass spectra of 10 samples might be recorded routinely within one hour and depending on resolution of using mass spectrometer, can be detected up to 60 elements simultaneously in each sample with detection limits 1 ppm or even far below. It means an analytical job for single element determination with ppm range of precision may take only 6 second.

In this work, the carcinogenic and toxic to human elements such as lead, cadmium, chromium, arsenic, thallium and other heavy contaminant elements were determined by LA-ICP-MS method in samples of oil and ochre paints belonging to bestselling brands in Ulaanbaatar city market places and results were compared with such as done on acryl and oil paint samples, produced and permitted for household use in Germany. Paints were selected as a test probes because in Mongolia a low income people intensively uses bright color paints to paint their homes, fences, furniture, not having any stated warning information about toxicity of using paints. This "painting all" phenomenon wide spread in Mongolia, probably because it gives to people in poverty some kind of psychological comfort, hiding their poverty behind bright colors.

II. EXPERIMENTAL DETAILS

Imported from China red, yellow, green, and blue color oil paints of Honglian, Chulei, and Shunshiyouqi brands (12 samples), 8 samples of dry powder ochre paint (Chinese origin, but exact names of producers are unclear), 3 samples oil paints of Russian brand name "Leningradskiye krasky", 10 samples of acryl and oil paints of German brands OBI, ICI Dulux, Classic, Boden Beschichtung, Delta (Dörken), Faust, Brillux Lacryl-PU were selected and bought as 1 or 0.5 kg canned ready to use pieces (Figure 1).

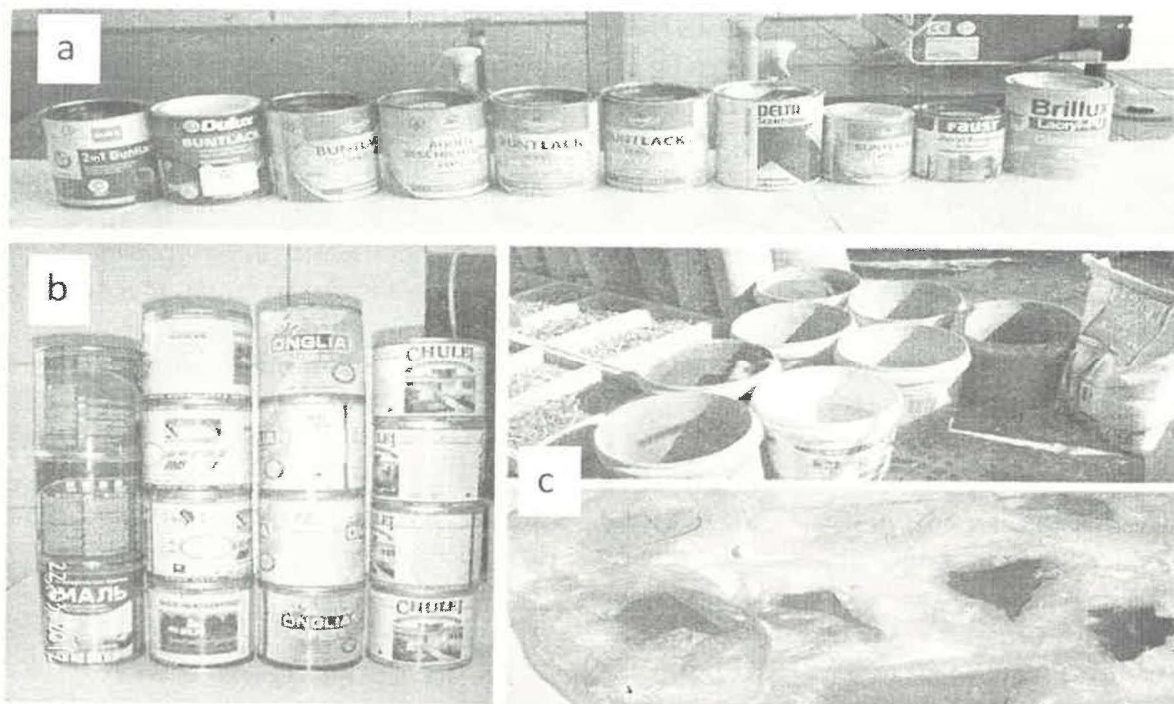


Figure 1. Selected to analysis paint samples. Produced and permitted in Germany household use purpose mostly acryl basea paints (a); bestselling in Ulaanbaatar city (Mongolia) Russian and Chinese brand name oil paints for indoor and outdoor works (b); Chinese origin water diluteable dry powder ochre paint for outdoor works (c).

Cans were shaken well before opening a lid to get drop of paint as an analyte probe. The analyte paint drops were then put on a 3x4.5 cm size glass substrate and were left to dry on a hot plate at least for 3 hour at 60⁰ C. During drying droplets turns into roundly shape 0.3-1 mm thick in center paint

spot, as shown on the Figure 2. Ochre paint powder samples were fixed on the surface of glass substrate diluting several milligram of the powder in molten drop of pure paraffin wax at 60⁰ C and then solidified by cooling to room temperature.

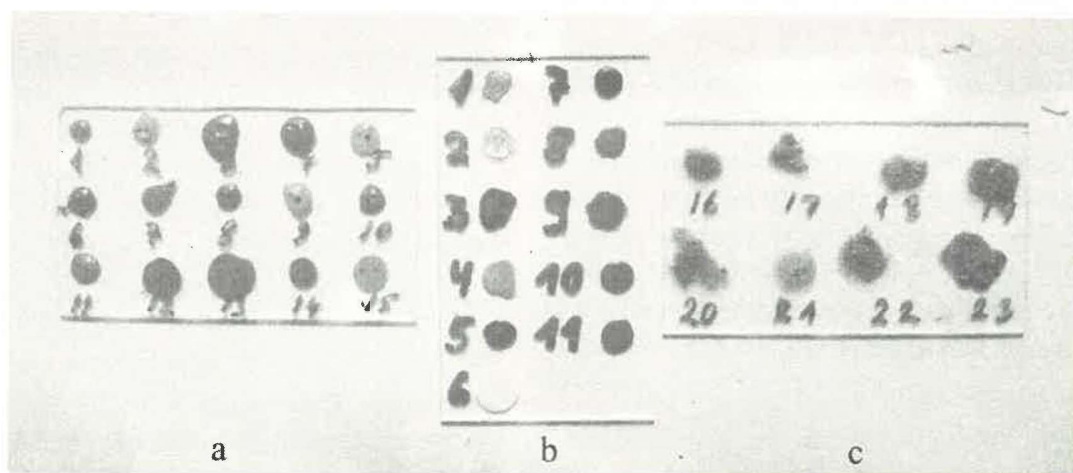


Figure 2. Analyte paint droplets on 3x4.4 cm glass substrates after drying on a hot plate. Chinese and Russian brand oil paints (a); German acryl and oil paints (b); Chinese origin dry powder ochre paint samples solidified with pure paraffin wax (c).

The substrate with analyte then was put into an air tight but argon flow cell and ablated through quartz window of the cell by 5 Hz repeating rate pulses of

193 nm wavelength laser beam from ArF eximer laser unit COMPEX (Lambda Physik, Germany). Single laser pulse energy density delivered onto the

120 μm diameter size sample surface area was around 5 J cm^{-2} , and was spatially well homogenized to ablate flat-bottom crater. A fine dust material ablated from the sample was transported through tubing by argon flow and feed ICP torch at the ion entrance of the quadrupole mass spectrometer ELAN DRC II (Perkin Elmer Sciex). The mass spectrums were visualized and processed in the Iolite v2.31 software application environment [11], based on the Igor Pro 6.22 data processing program [12]. Final concentrations of elements were calculated using Ca, Si as internal standard elements, because they were found in every sample. High amount of calcium sulfate or silicon dioxide (or both of them) always added in paints as hardening filler. The recorded in same condition mass spectra of the NIST610 glassy standard material was used as external reference. The NIST 610 standard which is accepted for analysis of geological samples was used because lack of any recognized reference material specially designed for paint analysis by ICP-MS or by LA-ICP-MS methods.

Any oil or acryl based paint consist of binder, solvent and pigment. Binder and solvent in most cases are a variety of organic substances, taking major part of paint mass. This organic part of paint consisting mostly of elements O, N, C, H, is impossible to detect if the ICP ionization technique is used to feed a mass spectrometer. It is simply because in this case ionization occurs in an air, the interfering media consisting of O and N, rich with C and H, in other hand, O, N, C, and H are atoms with quite high energy of ionization, and they tends withstand argon plasma temperature and not being ionized and lost at all being not counted.

So the LA-ICP-MS paint analysis is unable to give actual content of elements in paint, it gives the content that might be characterized as modified

or "organic matter ignored" content. This situation is main obstacle to recognize LA-ICP-MS paint analysis results as conclusive, but we hope that the analytical approach in this work will show quite accurate and high precision analysis is still possible with LA-ICP-MS for health and environment protection purposes paint analysis.

To find optimal detection accuracy and precision, time resolved mass spectra of oil and acryl paint samples were recorded ablating the sample by "drilling" hole and surface rastering way. The drilling hole means that laser beam pulses strike on same point of the sample surface and removes dried paint material layer by layer until the hole digging reaches glass substrate, the moment was immediately noticed by drastic increase of silicon and decrease of calcium ions counts on the recording *in situ* spectra. Any element content that calculated and found from drilling hole time integrated mass spectra represents average of different paint layer content of same element, but the averaged content refers only to the local microscopic position where the drilling was occurred, where local composition might be different from average of whole sample. In the rastering ablation, sample desk was moved in rectangle zigzag way during ablation, scan speed was selected as only 3 lasing pulses might shot the same point of the sample. In this way of ablation, mass spectra of 1 mm^2 macroscopic area is recorded and time averaged, but in this case calculated concentrations represents 30-50 μm thin surface layer, instead bulk of the paint sample. Magnified images of hole drilling and surface rastering after-ablation sites on the paint surface taken with Keyence VHX-600 Digital Microscope are shown on the Figure 3. The ochre paint mass spectrums were recorded only by surface rastering ablation, because of sufficient initial homogeneity of this kind of dry powder paints.

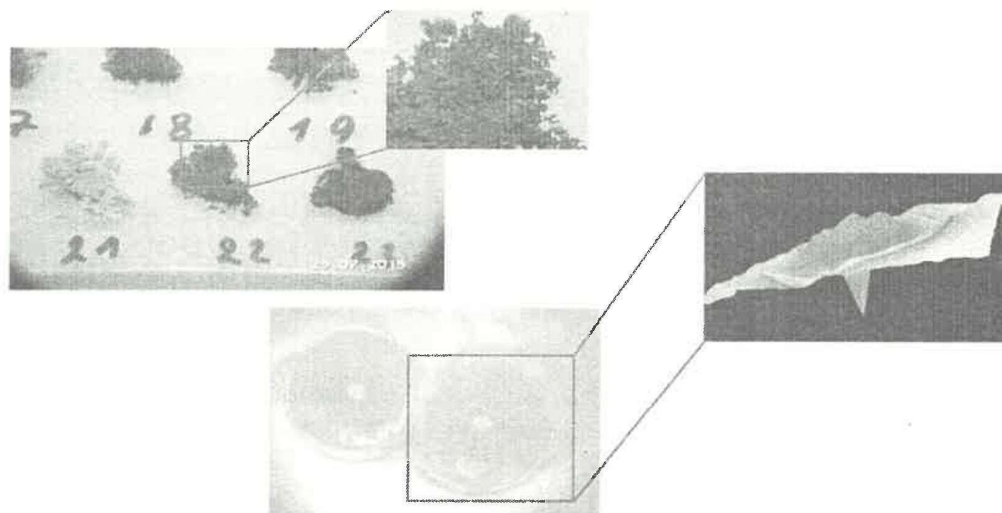


Figure 3. Magnified optical images of after-ablation sites on the paint surface taken with Keyence VHX-600 Digital Microscope. The upper image shows square-shape trace of laser ablation on the surface of ochre paint sample and lower image shows two holes drilled in an oil paint sample. The inset in the lower image is 3D digital recovery of one of holes depths profile. Conical shape of hole is formed due to softening of organic flesh of the oil paint sample by heat delivery of ablating laser pulses.

III. RESULTS AND DISCUSSION

The given in the Table 1 measured content of elements in ppm corresponds oil and acryl paint sample drilling ablation and ochre paint surface rastering ablation. Many elements such as most of rare earths, precious metals surely detected but in concentrations less than 10 ppm were ignored as trace and not shown in the table. Concentration values for health adverse or hazardous heavy elements such as As, Cd, Cr, Pb, Tl, Th, U were put in the table as they were detected even at trace level at the low detection limit edge.

As we mentioned previously, numbers in each column of the Table 1 must be adjusted being multiplied in some quantity, value of which depends on personal character of each element. These values must be determined once and adjusted with regular manner. As an example, we determined preliminarily lead and chromium content in first 23 paint samples given in the Table 1 by atomic absorption spectroscopy (AAS)

method and results were compared with that of determined by the LA-ICP-MS measurements. For the AAS measurements, each of 500 mg of liquid paint samplings were fully digested in mixture of acids using high pressure teflon bomb heated in microwave oven (Milestone 1200) in programmed way. The calculated correlation coefficients between AAS and LA-ICP-MS determinations were 0.85 for lead and 0.90 for chromium. These coefficients may be characterized as acceptable, if we consider that contents of lead and chromium in selected samples are cover 4-5 order wide range. As shows linear fit of two determination method (Figure 4), the LA-ICP-MS results are 9.3 times higher than that of given by the AAS for chromium, and 6.4 times higher for lead. So in general we should conclude that any element content directly determined in dried paint samples by LA-ICP-MS is around 5-10 times higher than actual content of the element.

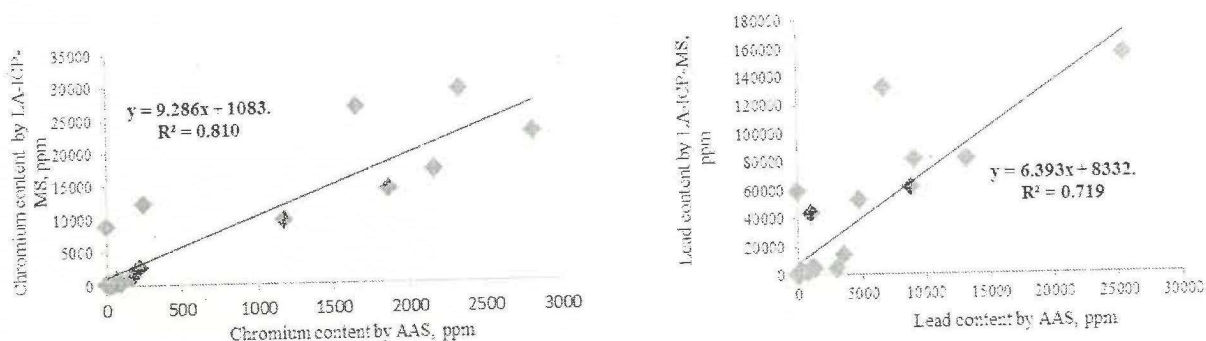


Figure 4. Linear fit between AAS and LA-ICP-MS determination of chromium (left) and lead (right) in the first 23 samples (see the Table 1). The correlation coefficients between results of two methods were 0.90 for chromium and 0.85 for lead.

The 2σ criteria relative standard deviation (RSD) of each element determination averaged through all set of samples depended inverse on content of elements. The average RSD of the mostly high content elements Ca, Al, Mn, Pb, Sr, S, Mg, Fe, Sb, Na, Co, Si, Zn, Cu, P, Y, K, Cl, Ce, and La is less than 10%, the RSD of elements Ti, Cr, Sn, Ba, Zr, Rb lies between 10 and 20%, and the RSD of trace elements Gd, Nb, Sc, V, U, Pr, Ni, Ga, Eu, As, Th, B, Mo, Cd, Li lies in interval from 20 to 50 %.

Oil paint sample surface ablation and drilling result comparison shows that dried oil paint surface is enriched in 10-20% with Si and Ti comparative to the bulk body of the paint, while paint bulk is 10-20 % enriched with Ca comparative to the surface. It may be related to layering during paint drying process, which is might be specially designed by producers of paints in way that silicon oxide is diffused to surface to become protective skin while calcium carbonate is lying inside to support organic flesh body of paint as bone skeleton.

As shows the Table 1, highest content inorganic elements in Chinese brand paints are Ca, Mg, and Ba, in the Russian brand oil paints the content of Ca is highest and exceed nearest content of Si at least ten times. In the German brand paint samples,

contents of these 3 elements are much lower but contents of Si, Ti, and Al are much higher than that of in Chinese or Russian paints, except detected 308000 ppm (or actually about 30800 ppm, if consider existence of paint organic matrix) content of Ba in the sample 29 (GER_Delta_oil_dark green). Any information about relative contents of inorganic macro components in paints might be useful when origin of paint sample is unknown and desired to know, but within this work we are more interested in either these paints contain harmful to human health elements as Pb, Cr, As, Cd or not, and if contains, how much impact it may have. Historically carbonates, oxides, sulfides of Pb, Cr, As, and Cd such as PbCO_3 (lead white), PbCrO_4 (chrome yellow), CdS (cadmium yellow), As_2S_3 (arsenic yellow) were popular pigments for a centuries. Nowadays toxicity of these elements and their compounds are well evidenced and proven, and in most of developed countries such a hazardous pigments allowed to use for outdoor painting, in artwork, or used to protect heavy duty machinery that works in aggressive environment. For example, the US Consumer Product Safety Commission (CPSC) is banned lead containing paints for any indoor environment design use since 1978.

Table 1. Measured content of elements in paint samples given in ppm and shown in sequence from highest to lowest average content. Sample name abbreviated as: CHN, RUS, GER (paint sample country of origin) _Hong, Chul, Shun... (paint sample brand name—see the text) _oil, ochre, acryl (paint type) _red, yell, grn, blue... (paint color in sequence of visible spectra).

[illegible]

Extracted from the Table 1 contents of elements Pb, Cr, As, Cd in ppm are shown graphically in the Figure 5. Measured lead content in the red, yellow, and green color Chinese brand paints (samples 2,3, 5-7, 9-11, 13-15) are high as 1980 - 154900 ppm or dividing by organic matrix coefficient 6.4 we found actual concentrations as 309 - 24300 ppm (mg/kg). In the Chinese blue color paints actual content of lead were surprisingly low as below 106 ppm. The actual contents of lead in

the Russian oil paints are also quite high as 408-933 ppm. The lead actual contents in the German paint samples were lowest and not exceed 2 ppm except the sample 29 (GER_Delta_oil_dark green) which contains lead at 18 ppm. Therefore the selected to investigate in this work Chinese and Russian origin certain brand red, yellow, and green color paints may be used only for outdoor works.

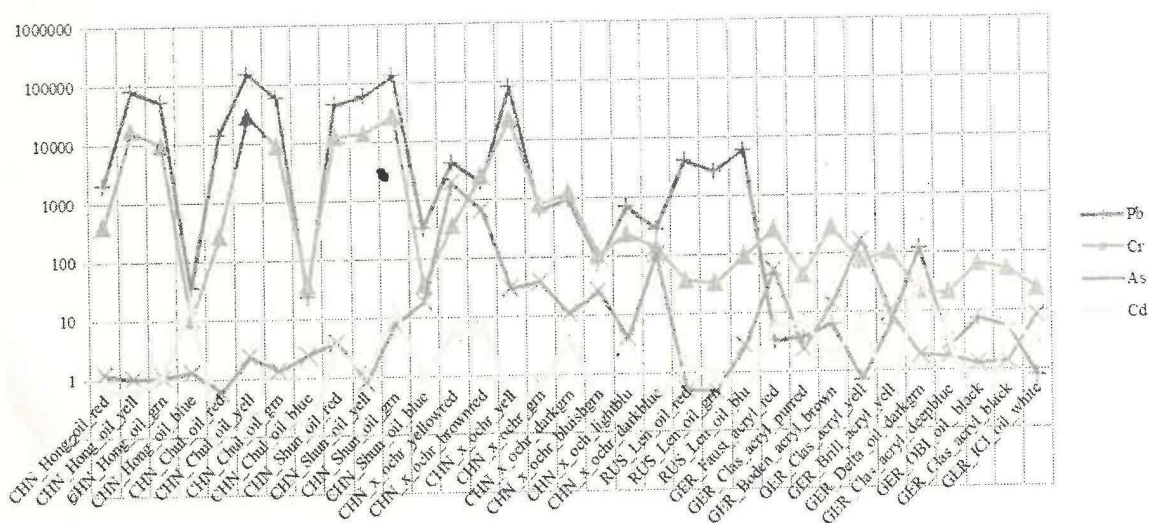


Figure 5. Measured by LA-ICP-MS method content of lead (Pb), chromium (Cr), arsenic (As), and cadmium (Cd) in paint samples given in ppm. Paint samples grouped by country of origin, brand name and put in sequence inside of each group in accordance with natural spectral sequence of colors: red-yellow-green-blue. Sample name abbreviations are same as in the Table 1.

As shows Figure 5, chromium content is also very high in above mentioned Chinese brand paints, actual contents lying between 29-3134 ppm, specially, yellow and green color oil paints contains more than 950 ppm of chromium. The Russian and German paints contain chromium moderately in range of 2-30 ppm, mostly below 10 ppm, except the samples 24 and 26.

Six valent chromium (Cr⁶⁺) is well known human carcinogen. In accordance with the US Environmental Protection Agency (EPA) standard, chromium tolerable exposure per a day for an adult male is 35µg/day; for an adult female is 25µg/day. According to the EPA, chromium content in drinking water must be below 0.1 mg/l [13, 14] and in accordance with the US Occupational Safety and Health

Administration (OSHA) chromium in dust air must be below 5 µg/m³ [15].

Painting floors with yellow color oil paint is wide spread practice in Mongolia. As shows numbers in Table 1 above, due to this practice, classroom indoor air might be constantly contaminated with chromium and lead. For example, classroom floors in ordinary high schools in Mongolia are repainted each year during summer vacation time. If suppose 5 kg of Chinese brand oil paint spending each summer for repainting of floor of classroom, a paint chips that scraps from the floor and might spread in classroom air as a microscopic dust particles will be also 5 kg or less during one academic year. It will contain 4.75g (950 ppm * 5 kg) of chromium, and if suppose 180 days of classwork

per an academic year, the floor of classroom will produce per a day a moveable with dust chromium amount 750 times ($4.7 \text{ g} / (35\mu\text{g/day}) * 180 \text{ day}$) as the EPA per a day standard for adult male.

As seen from the Table 1, a cadmium measured content is below 10 ppm in most of samples, which means the actual contents around 1 ppm or below. Blue and green color paint samples 4, 11, 29 contains correspondingly 17, 13, and 35 ppm of cadmium as highest measured. Cadmium and compounds of cadmium are classified as B1 group human carcinogens. The EPA estimates tolerable concentration (TC) of cadmium in air as $0.06 \mu\text{g}/\text{m}^3$ for an inhalation exposure, and TC for a dietary exposure 0.001 mg per a kg of body weight, per a day [16]. So the certain brand green and blue color paints might become low power but long term source of cadmium exposure.

The measured arsenic content in most of oil and acryl paints were below 10 ppm or actually below 1 ppm. But in the Chinese origin yellowish red and brown red ochre paints samples 13 and 14, very high amount of arsenic is detected correspondingly at 1897 and 638 ppm. Arsenic is the high toxic poison and classified as a group A human carcinogen, so the EPA is defined arsenic tolerable daily level goal as zero [17]. But completely removing arsenic from all human habitation environments is still impossible. So the EPA currently established arsenic TC in drinking water low as $10 \mu\text{g}/\text{l}$, TC in air as $2 \mu\text{g}/\text{m}^3$. The produced in China ochre paints not only contains high amount of all three strong contaminants lead, chromium, and arsenic, they are also contains sub ppm but surely detected amount of thallium and thorium. So these ochre paints are dangerous enough to classify them just as poisons.

Arsenic is detected in German brand acryl red and yellow color paint samples 24 and 27 in notable concentrations: 53 ppm and 165 ppm. So any item painted with these paints might become significant contaminant source of arsenic.

IV. SUMMARY

The LA-ICP-MS method is possible to use as express semiquantitative detection method for most of inorganic additives in oil, acryl and ochre paints using glassy standard sample.

High level of concentration 309 – 24300 ppm for lead, 950- 3134 ppm for chromium are detected by LA-ICP-MS method in samples of red, yellow and green color oil paints produced in China and bestselling in Mongolia certain brand products. Up to 1900 ppm alarming high content of arsenic is found in the Chinese origin yellowish red, brown red color ochre paints.

The discovered high level of lead, chromium and arsenic in certain brand paints is concerning fact. As shows our analyses results, the red, yellow and green color paints of certain brand name produced in China, might be hazardous and even dangerous if they will be used to paint interior of public and residential house buildings which will create potentially contaminated indoor environment to human.

The certain brand Chinese origin yellow and red oil and all kind of ochre paints better to be banned at all. Such a measure surely will have significant impact on reducing of health adverse effect caused by presence of these elements in every day human environment in countries like as Mongolia.

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REFERENCES

1. <http://lc.gov.mn/law/class/101/detail/1003230002/>
2. Laser Ablation-ICP-MS in the Earth Sciences. CURRENT PRACTICES AND OUTSTANDING ISSUES. Edited by Paul Sylvester,

Department of Earth Sciences, Memorial University of Newfoundland, A1B 3X5, Canada, 2008.

3. Steven F. Durrant and Neil I. Ward. Recent biological and environmental applications of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), *J. Anal. At. Spectrom.*, 2005, 20, 821-829.
4. Johanna Sabine Becker, Carola Pickhardt, Hans-Joachim Dietze. Laser ablation inductively coupled plasma mass spectrometry for the trace, ultratrace and isotope analysis of long-lived radionuclides in solid samples. *International Journal of Mass Spectrometry* 202 (2000) 283-297.
5. Carola Pickhardt, Hans-Joachim Dietze, J. Sabine Becker. Laser ablation inductively coupled plasma mass spectrometry for direct isotope ratio measurements on solid samples. *International Journal of Mass Spectrometry* 242 (2005) 273-280.
6. W. D. James, E. S. Dahlin, D. L. Carlson. Chemical compositional studies of archaeological artifacts: Comparison of LA-ICP-MS to INAA measurements. *Journal of Radioanalytical and Nuclear Chemistry*, Vol. 263, No. 3 (2005) 697-702.
7. Isolde Deconinck, Christopher Latkoczy, Detlef Gunther, Filip Govaert and Frank Vanhaecke. Capabilities of laser ablation—inductively coupled plasma mass spectrometry for (trace) element analysis of car paints for forensic purposes. *Journal of Analytical Atomic Spectrometry*, 2006, 21, 279-287.
8. Andria L. Hobbs, José R. Almirall. Trace elemental analysis of automotive paints by laser ablation—inductively coupled plasma—mass spectrometry (LA-ICP-MS), *Anal Bioanal Chem* (2003) 376 : 1265-1271.
9. Yi-Ling Lee, Chao-Chiang Chang, Shiuh-Jen Jiang. Laser ablation inductively coupled plasma mass spectrometry for the determination of trace elements in soil. *Spectrochimica Acta Part B* 58 (2003) 523-530.
10. D. Brophy, T. E. Jeffries, B. S. Danilowicz. Elevated manganese concentrations at the cores of clupeid otoliths: possible environmental, physiological, or structural origins. *Marine Biology* (2004) 144: 779-786.
11. http://iolite.earthsci.unimelb.edu.au/wiki/doku.php?id=manual_page
12. <http://www.wavemetrics.com/>
13. John B. Vincent, Recent advances in the nutritional biochemistry of trivalent chromium, *Proceedings of the Nutrition Society*, 63 (1), pp 41-47, 2007.
14. <http://water.epa.gov/drink/info/chromium/index.cfm>

15. http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=STANDARDS&p_id=13216
16. <http://www.epa.gov/ttn/atw/hlthef/cadmium.html>
17. <http://www.epa.gov/ttn/atw/hlthef/arsenic.html>