Kohl containing lead (and other toxic elements) is widely available in Europe

Filella, M

http://hdl.handle.net/10026.1/15960

10.1016/j.envres.2020.109658
Environmental Research
Elsevier BV

Kohl containing lead (and other toxic elements) is widely available in Europe

Montserrat Filella[a], Agathe Martignier[b], Andrew Turner[c]

[a]Department F.-A. Forel, University of Geneva, Boulevard Carl-Vogt 66, CH-1205 Geneva, Switzerland

[b]Department of Earth Sciences, University of Geneva, CH-1205 Geneva, Switzerland

[c]School of Geography, Earth and Environmental Sciences, University of Plymouth, Drake Circus, Plymouth PL4 8AA, UK

Accepted 8th May 2020

https://doi.org/10.1016/j.envres.2020.109658

Abstract

Kohl is an eye cosmetic that was traditionally used in many Asian and African countries but that is now more widely available. Ingredients of kohl reported in previous studies seem to be rather variable but mention is frequently made of minerals based on Pb whose use in cosmetic products is prohibited in Europe. We purchased 23 products of kohl from retail outlets in five different European countries and over the internet and analysed their chemical composition by XRF and SEM-EDXS. The majority of the products (n = 17) did not conform with European legislation based on the presence of Pb (often as galena), whose concentrations ranged from a few mg kg^{-1} to over 400000 mg kg^{-1}. Lead appeared to be present as galena in many cases. Cadmium, another element prohibited in cosmetic products in Europe, was also present as a contaminant in 13 products at concentrations up to a few hundred mg kg^{-1}. In addition to heavy metals, minerals of other metals (e.g. Fe and Zn) appeared to be present in the nano-size range and might represent an additional health hazard. Clearly, the lack of quality control in the manufacture of kohl results in the widespread occurrence of toxic and unwanted elements and the trade of illegal products in Europe. In principle, shop sales would be relatively straightforward to prevent, but products traded through internet are more difficult to regulate.

Keywords: kohl; XRF; SEM-EDXS; lead; cadmium; toxicity

1. Introduction

Kohl is an eye cosmetic that has been used since antiquity to darken the eyelids and as mascara for the eyelashes. It is documented to have been used by ancient Egyptians as a cosmetic and as a medicinal collyrium (Ebers Papyrus, c. 1550 BCE; Hirschberg, 1982). Kohl is still in use in the Middle East, the north and Horn of Africa, the Indian subcontinent (India, Iran, Pakistan, Bangladesh, Nepal), and southern regions of the former Soviet Union. Depending on geographical area, different terms are used to name similar products (e.g., kajol, al-kahal, surma, tiro, kwalli) but we will only use the generic term kohl in this study. It should be noted, however, that the term kohl has been adopted by some commercial cosmetic firms for some mascara products that bear no relationship with the 'ethnic' kohl products discussed here.

In the literature regarding the metalloid, antimony (Aldersey-Williams, 2011; Schwarz-Schampera, 2014), and in much of the literature about Arab cultural traditions ancient kohl is identified with stibnite (Sb_2S_3). More recently, however, the composition of kohl appears to vary widely and lead sulphide seems to be commonly present (Table SI1). It has been suggested that the originally used Sb sulphide was gradually substituted by Pb sulphide because Sb became scarce and too expensive (Al-Hazzaa and Krahn, 1995; Hardy et al., 1998; Vaishnav, 2001; Al-Ashban et al., 2004; Jallad and Hedderich, 2005) but no author appears to provide a precise timeline. Interestingly, evidence gathered towards the end of the nineteenth century by Fischer (1892) and corroborated by more recent analyses points to Pb as the main constituent of Egyptian eye preparations rather than Sb (Walter et al., 1999). Some authors assert that the confusion might arise from the closeness of the Egyptian name for lead sulphide, galena (*stim*) and the Latin name for antimony (*stibium*) (Mahmood et al., 2019).

Traditionally, the kohl powder is applied to the conjunctive surface of the eyelids in the same way as mascara is applied to the outer surface for a variety of reasons: to make the eyes beautiful; as a daily tradition stemming from both cultural and religious backgrounds; and for its perceived therapeutic properties. It is also applied to the umbilical stump of newborn babies, to the eyes of babies and infants to 'improve' eye health and to protect them against 'bad eye', and to stop bleeding after newborn circumcision. The use of Pb-containing kohl, particularly in children, has been repeatedly associated with high Pb concentrations in blood, with excellent reviews provided by Tiffany-Castiglioni et al. (2012) and, from a more historical perspective, by De Caluwé (2009).

Kohl is now also used by immigrant Asian populations in western countries. The first warning of the implication of kohl as a cause of Pb poisoning among the Asian community in the UK was issued by Warley and co-workers more than 50 years ago (Warley et al., 1968). The case described an Asian child in London with Pb encephalopathy and led to a warning from the Home Office asking for a voluntary sale restriction in 1968. The subject continued to gain attention in the UK in the 1970s (Betts et al., 1973; Snodgrass et al., 1973; Josephs, 1977; Ali et al., 1978; Aslam et al., 1979; Green et al., 1979) but interest subsequently waned. The presence of Pb was also reported in cosmetics bought in the US nearly 30 years ago (Parry and Eaton, 1991) and resulted in a request for a control of lead "originating from a variety of unorthodox sources". In continental Europe, the presence of Pb in kohl products has been more sparsely documented, with isolated studies conducted in Denmark (Bernth et al., 2005), France (Sainte et al., 2010; Kervegant et al. 2012) and Belgium (Bruynel et al., 2002).

In the US, kohl is defined as a colour additive and is not permitted in cosmetics or in any other FDA-regulated product (FDA, 1996, 2001). Kohl is not specifically regulated as such in Europe but Pb and its compounds have been banned in cosmetics since 1976 (Council of the European Communities, 1976) and are subjected to current European legislation for cosmetics (European Parliament and Council of the European Union, 2009). According to the EC legislation, the main regulatory framework for finished cosmetic products when placed on the EU market, elements that cannot be present are Sb, Cd, Pb and Se (with the exception of SeS_2 in antidandruff shampoos), with the presence of Zn also controlled.

In the frame of our research on the presence of toxic elements such as Pb and Sb in consumer products (Turner and Filella, 2017; Turner, 2018), we have investigated the availability and characteristics of kohl in Europe that does not comply with EC legislation on cosmetics. We have combined measurements of two complementary techniques: portable x-ray fluorescence (XRF) spectrometry and scanning electron microscopy-energy-dispersive x-ray spectroscopy (SEM-EDXS). While XRF provides a rapid semi-quantitative chemical composition of the whole sample, SEM-EDXS yields an insight into the aspect and visual heterogeneity of the analysed objects at the microscale range accompanied by the possibility of performing semi-quantitative analysis of individual components of the samples.

2. Materials and Methods

Products were purchased in Europe through retail shops in Belgium, France, Spain, Switzerland and the UK or via the internet (Amazon.de, Amazon.uk, eBay) and delivered to Luxembourg or the UK. All samples were coded, photographed in their original packaging and any details of composition and origin noted.

2.1 XRF analysis

A battery-operated Niton XL3t 950 He GOLDD+ portable XRF spectrometer housed in a laboratory accessory stand and remotely operated via a laptop was used for XRF analysis. Between 2 and 5 g of powdered samples, pastes or kohl stones (used to manually prepare kohl) purchased in jars or bottles were transferred to polyethylene XRF cups (Chemplex series 1400; 21-mm internal diameter) and collar-sealed with 3.6 μm SpectraCertified Mylar polyester film; softer material in kohl pencils or sticks (50 to 100 mg) was scraped directly onto Mylar film. Measurements of elements of atomic mass $\geq$ 40 were conducted in a mining mode and with a beam width of 8 mm for a total time of 60 s, comprising successive counting periods of 30 s at 50 kV/40 μA (main filter), 15 s at 20 kV/100 μA (low filter) and 15 s at 50 kV/40 μA (high filter). Elemental concentrations (in mg kg^{-1}) were derived from fluorescent x-ray spectra using fundamental parameters encoded in the Niton Data Transfer software. The performance of the instrument was checked by measuring two certified reference sediments (NIST 2709 and GBW07318) contained in XRF cups with each batch of samples. Detection limits for the kohl samples, based on the lowest counting errors multiplied by three, ranged < 20 mg kg^{-1} for As, Pb and Rb to about 150 mg kg^{-1} for Ba, Mn, Sn, Ti.

2.2 SEM-EDXS analysis

While XRF provides the elemental composition of whole samples (or areas of 8 mm in diameter), EDXS measurements are performed on a volume of 2 to 3 μm in diameter that targets specific grains or groups of grains.

For EDXS, samples of kohl were mounted on aluminium stubs using double-sided conductive carbon tape and coated with Au (ca. 10 nm) using low vacuum sputter coating. A JEOL JSM-7001F scanning electron microscope, equipped with an EDXS detector (model JEOL EX-94300S4L1Q), was used to perform analyses and to obtain secondary electron images of the samples. Imaging was also accomplished with backscattered electrons where elements with high atomic number appear brighter in the image. EDXS measurements were acquired with an accelerating voltage of 15 kV, a beam current of 7 nA and an acquisition times of 30 s. Semiquantitative EDXS analyses of elemental concentrations were made without taking C, N and O into account (elemental quantification is not as good for light elements). The presence of C can nevertheless clearly be identified in the EDXS spectrum by the presence of a peak at 0.27 keV representing the characteristic carbon K_{α} line. EDXS results are all presented as mol %, with detection limits dependent on several parameters but estimated to be around 1%.

3 Results

Information about the 23 samples studied is shown in Table 1, with content data available on the container or packaging given where available. Table SI2 shows pictures of the samples as purchased and illustrates that some products are sold under different names depending on the provider and country of purchase (for example, compare samples #5 and #6, and samples #2, #9 and #10). All products are black or grey, with the exception of a blue pencil (# 12), and exhibited a variety of textures and lustres. Some products are powders, some are pastes, a few are sticks or pencils with a soft interior, and two are 'kohl stones' used to prepare final products either at home or by local retailers.

The elemental compositions of the kohl samples (atomic mass $\geq$ 40) as obtained by XRF analysis are shown in Table 2 and SI3 and reveal marked variations in chemical makeup. Lead is detectable in 17 out of the 23 products tested and three distinct groups can be observed. Thus, some samples contain very high concentrations of Pb in the 400000 mg kg^{-1} range (# 1, 3, 13, 18, 19, 23) and some samples contain high concentrations of Pb in the 25000-40000 mg kg^{-1} range (# 20, 21, 22), while remaining samples exhibit low concentrations of Pb in the approximate range of 40 to 1400 mg kg^{-1} (# 2, 6, 7, 8, 9, 10, 15, 17). The first two groups point to a Pb mineral being the main constituent, either alone or mixed with other compounds, while the third group suggests that Pb is present as a contaminant. Cadmium is detectable in 12 kohl samples over a concentration range of 14.5–369 mg kg^{-1}, with concentrations above 160 mg kg^{-1} always associated with Pb-rich samples. Iron and zinc are detected in a total of 18 and 17 samples, respectively, with concentrations ranging two or three orders of magnitude and from about 100 to 77000 mg kg^{-1} for Fe and about 100 to 40000 mg kg^{-1} for Zn. It would appear, therefore, that some samples contain either a Fe or Zn mineral as the main, or as an important, component. While some samples were relatively 'clean' with respect to the aforementioned elements (# 8, 14, 16), a general characteristic of the products is that they all contain traces of an array of unwanted chemical elements like Ba, Co, Cr, Cu, Ni, Sb, Sn and W.

Although SEM-EDXS does not provide quantitative measurements on whole kohl samples, it provides information on the structure and particle size of the materials and a semi-quantitative analysis of selected objects and as such is complementary to XRF. Images derived from this approach are shown in the SI file and a summary of the observations is given in Table 3. SEM-EDXS confirmed the variety of products sold under the kohl umbrella as well as the heterogeneous composition of most products. As explained above, EDXS cannot provide semi-quantitative information on C but a distinctive peak at 0.27 eV in a few samples (#s 11, 14, 16) suggests material of an organic matrix.

Some samples contained a Pb-S mineral that was often mixed with other components (#s 1, 3, 13, 18, 19, 20, 21). This compound revealed stoichiometries of Pb:S of 60:40, 66:34 or 69:31 and appeared as well-defined cubes (Figure 1a, 1b and 1f), embedded in other matrices (Figures 1c and 1d), or as very small particles covering a larger one (Figure 1e and 1f). Galena, a PbS mineral, is typically cubic, octahedral or a combinations of the two, and it would be reasonable to assume that the compound we observe is this. Note that the inconsistencies in the stoichiometries observed above and the stoichiometry of pure galena may be attributed to instrument response (e.g., an underestimation of the quantity of S, a relatively light element) and/or surface oxidation and the formation of secondary minerals like Pb sulphate and Pb carbonate

Aluminosilicates and Si-Mg and Si-Na compounds were present in a number of kohl samples. The Si-Mg compound could be talc, whose presence has already been mentioned in previous studies (Table SII). Also of interest is the presence of metal oxides in the nano-size or micro-size range (Zn, #s 4, 6; Cu, # 12; Fe, #s 5, 11) that were located using backscattered images, and as exemplified in Figure 2. In other cases, the presence of Zn and Fe were registered without nano-particles being spotted (#s 2, 9, 17).

Overall, there is good agreement between the results of the kohl sample analyses arising from XRF and SEM-EDXS.

4. Discussion

From the compositional perspective, our results confirm those of previously published studies that have investigated the makeup of kohl (Table SI1). Our findings are, however, both surprising and cause for concern in that so many products that are readily available for purchase in Europe at retail outlets and through the internet contain very high concentrations of Pb. While some of the products containing the highest levels of Pb do not provide quantitative or qualitative information on kohl composition, others give information that is not accurate or that is misleading. For instance, two products containing Pb at above 40% by weight declare or imply the contents to be 'lead-free', with one of the products referring to an Sb-based material when the metalloid was not detected by our XRF analysis (Sb was only found at trace levels in four products). The labelling of another product states that no Pb is present according to laboratory tests but contains well over 1000 mg kg^{-1} of the heavy metal according to XRF. SEM-EDXS results suggest that high levels of Pb across a range of products and texture types that are manufactured in different countries throughout Asia and Africa arise from the common use of the sulphidic mineral, galena.

An additional concern unveiled by our study is that most kohl products analysed not only contain lead but also a heterogeneous array of other chemical elements, including the heavy metal Cd, that is also highly toxic. This suggests that these products lack any quality control during material sourcing and manufacture and are produced from low-grade and impure materials. This problem may be more acute than our results indicate because portable XRF is not a particularly sensitive technique and many of the elements we analysed may be distributed in a larger number of samples at lower concentrations. Based on the detection of Pb and/or Cd by our XRF analyses, 21 out of 23 products are non-compliant with respect to current European legislation.

SEM observations also reveal an extremely heterogeneous particle size distributions, often with very small particles present. Of potential significance from a toxicological viewpoint, therefore, is the presence of some metal compounds, such as Zn oxide, at the nano- or micro-sized particle range. Apart from the problems directly associated with the higher solubility of very small particles in the eyes and mouth, exposure to potentially harmful elements can also take place via the respiratory system, if particles below PM10 or PM2.5 present in many of the products investigated were to become airborne. Concerns about the presence of minerals in the nanosize range in cosmetics usually refer to ZnO, a widely used ingredient in sunscreens (Kim et al., 2017), but in kohl products nano-sized particles composed of a variety of additional elements (including Pb and Cd) may be present.

The presence of seemingly non-toxic compounds such as talc might also be problematic from a health perspective. Pure talc itself has been implicated in various respiratory illnesses (Wild et al., 2008) but is not currently classified as carcinogenic according to the IARC (American Cancer Society, 2020). However, given the apparent lack of quality control in the manufacture of the kohls referred to above, the presence of talc could be associated with the occurrence of more harmful asbestos (Rohl et al., 1976).

Summary

The results obtained in this study indicate that kohl products available in Europe, but manufactured elsewhere, have a very physical and chemical heterogeneous composition and that many of them contain significant amounts of toxic elements like, Pb and Cd, whose presence is not permitted according to current European legislation. Such products used to be obtained by European-based users through friends and relatives (Ali, 1978) but now they are either imported and sold in retail shops or purchased via the internet. While, in principle, shop sales would be relatively straightforward to prevent, that products can be so readily obtained through internet sources is particularly worrisome. More generally, the study confirms that the internet is an essentially unregulated market for consumer goods with health and safety regulations that are either virtually absent or unenforced.

Funding

This research did not receive any specific grant from funding agencies in the public, commercial or not-for-profit sectors.

References

Al-Ashban, R.M., Aslam, M., Shah, A.H., 2004. Kohl (surma): a toxic traditional eye cosmetic study in Saudi Arabia. Public Health 118, 292–298.

Aldersey-Williams, H., 2011. Periodic Tales. The Curious Lives of the Elements. Penguin Books.

Al-Hazzaa, S.A.E., Krahn, P.M., 1995. Kohl: a hazardous eyeliner. Int. Ophthalmol. 19, 83–88.

Ali, A.R., Smales, O.R.C., Aslam, M., 1978. Surma and lead poisoning. Br. Med. J. 2 (6142), 915–916.

American Cancer Society, 2020. Talcum Powder and Cancer. https://www.cancer.org/cancer/cancer-causes/talcum-powder-and-cancer.html. Last accessed 3/20.

Aslam, M., Davis, S.S., Healy, M.A. 1979. Heavy metals in some Asian medicines and cosmetics. Public Health London 93, 274–284.

Bernth, N., Hansen, O.C., Hansen, S.F., Pedersen, E., 2005. Survey of chemical substances in kohl and henna products. Survey of Chemical Substances in Consumer Products, No. 65. Danish Environmental Protection Agency.

Betts, P.R., Astley, R., Raine, D.N., 1973. Lead intoxication in children in Birmingham. Br. Med. J. 1, 402–406.

Bruyneel, M., De Caluwé, J.P., des Grottes, J.M., Collart., F., 2002. Usage de khôl et intoxication saturnine grave à Bruxelles [Kohl use and severe lead poisoning in Brussels]. Rev. Med. Brux. 23, 519–522.

De Caluwé, J.-P., 2009. Intoxication saturnine provoquée par l’usage prolongé de khôl, une cause sous-estimée dans les pays francophones [Lead poisoning caused by prolonged use of kohl, an underestimated cause in French-speaking countries]. J. Fr. Ophtalmol. 32, 459–463.

Council of the European Communities, 1976. Council Directive of 27 July 1976 on the approximation of the laws of the Member States relating to cosmetic products (76/768/EEC), Official Journal of the European Communities L 262/169.

European Parliament and Council of the European Union, 2009. REGULATION (EC) No 1223/2009 of the European Parliament and of the Council of 30 November 2009 on cosmetic products. Official Journal of the European Union L 342/59.

FDA, 1996. Import alert no. 53-13, Automatic detention of eye area cosmetics containing Kohl, Kajal or Surma, Revised 1/26/96. US Food and Drug Administration (www.fda.gov).

FDA, 2001. Eye cosmetics safety. US Food and Drug Administration, Office of Cosmetics and Colors Fact Sheet, August 1, 2001 (www.cfsan.fda.gov).

Fischer, X., 1892. Die chemische Zusammensetzung altägyptischer Augenschminken [The chemical composition of ancient Egyptian eye preparations]. Arch. Pharm. 230, 9–38.

Green, S.D.R., Lealman, G.T., Aslam, M., Davies, S.S., 1979. Surma and blood lead concentrations. Public Health London 93, 371–376.

Hardy, A.D., Vaishnav, R., Al-Kharusi, S.S.Z., Sutherland, H.H., Worthing, M.A. 1998. Composition of eye cosmetics (kohls) used in Oman. J. Ethnopharmacol. 60, 223–234.

Hirschberg, J., 1982. The History of Ophthalmology, Vol. 1: Antiquity. Verlag J. P. Wayenborgh, Bonn.

Jallad K.N., Hedderich H.G. 2005. Characterization of a hazardous eyeliner (kohl) by confocal Raman microscopy. J. Hazard. Mater. B124, 236–240.

Josephs, D.S., 1977. Abnormal exposure to lead and anaemia in Luton Asian children. Public Health London 91, 133–140.

Kervegant, M., Glaizal, M., Tichadou, L., Hayek-Lanthois, M., de Haro, L., 2012. Risque d’imprégnation par le plomb lors d’usage quotidien de khôl [Daily use of kohl at the origin of possible lead poisoning]. La Presse Médicale 41, 203–204.

Kim, K.-B., Kim, Y.W., Lim, S.K., Roh, T.H., Bang, D.Y., Choi, S.M., Lim, D.S., Kim, Y.J., Baek, S.-H., Kim, M.-K., Seo, H.-S., Kim, M.-H., Kim, H.S., Lee, J.Y., Kacew, S., Lee, B.-M., 2017. Risk assessment of zinc oxide, a cosmetic ingredient used as a UV filter of sunscreens. J. Toxicol. Environ. Heal. B 20, 155–182.

Mahmood, Z.A., Zoha, S.M.S., Usmanghani, K., Hasan, M.M., Ali, O., Jahan, S., Saeed, A., Zaihd, R., Zubair, M., 2009. Kohl (surma): retrospect and prospect. Pak. J. Pharm. Sci. 22, 107–122.

Parry, C., Eaton, J., 1991. Kohl: a lead-hazardous eye makeup from the Third World to the First World. Environ. Health Perspect. 94, 121–123.

Rohl, A.N., Langer, A.M., Selikoff, I.J.,Tordini, A., Klimentidis, R., Bowes, D.R., Skinner, D.L. 1976. Consumer talcums and powders: Mineral and chemical characterization. J. Toxicol. Environ. Heal. 2, 255–284.

Sainte, C., Gille, S., Montout, P., Droguet, C., Coursimault, A., Fargette, B. 2010. Utilisation des khôls traditionnels, une source sous-estimée de saturnisme infantile—analyse élémentaire de dix-huit khôls traditionnels par ICP-AES et spectrométrie de fluorescence X [Use of kohl, an underestimated cause of childhood lead poisoning – measurementsof content with wavelength dispersive X-ray spectrometry analysis and an ICP-OES spectrometer]. Ann. Toxicol. Anal. 22, 181–185.

Snodgrass, G.J.A.I., Ziderman, D.A., Gulati, V., Richards, J. 1973. Cosmetic plumbism. Br. Med. J. 4, 230.

Schwarz-Schampera, U., 2014. Antimony. In: Gunn, G. (Ed.), Critical Metals Handbook. Wiley, Chichester, pp. 70–98.

Tiffany-Castiglioni, E., Barhoumi, R., Mouneimne, Y. 2012. Kohl and surma eye cosmetics as significant sources of lead (Pb) exposure. Glob. J. Health Sci. 1 http://dx.doi.org/10.5339/jlghs.2012.1

Turner, A., 2018. Black plastics: Linear and circular economies, hazardous additives and marine pollution. Environ. Int. 117, 308–318.

Turner, A., Filella, M., 2017. Field-portable-XRF reveals the ubiquity of antimony in plastic consumer products. Sci. Total Environ. 584–585, 982–989.

Vaishnav, R., 2001. An example of the toxic potential of traditional eye cosmetics. Indian J. Pharmacol. 33, 46–48.

Walter, P., Martinetto, P., Tsoucaris, G., Bréniaux, R., Lefebvre, M.A., Richard, G., Talabot, J., Dooryhee, E., 1999. Making make-up in ancient Egypt. Nature 397, 483–484.

Warley, M.A., Blackledge, P., O´Gorman, P. 1968. Lead poisoning from eye cosmetics. Br. Med. J. 1, 117.

Wild, P., Leodolter, K., Réfrégier, M., Schmidt, H., Bourgkard, E., 2008. Effects of talc dust on respiratory health: results of a longitudinal survey of 378 French and Austrian talc workers. Occup. Environ. Med. 65, 261–267.

Table 1. Description of the products analysed. Photographs of the products are shown in Figure S1.

ID	Product	Origin	Date of purchase	Information as provided in the products
1	Kohl Ithmid by SunnaHealing UK	Bought from Amazon UK, delivered in UK; delivery offered in other countries	22 June 2019	Lead-free antimony according to Amazon webpage; no composition given
2	Kohl Al-Sherifan	Bought in a shop in Madrid, Spain Origin unknown	28 May 2019	Free from lead Active ingredients: Sankh (42.5 %), Sufoof-E-Syah (42.5 %), Bhimseni Kafoor (15 %)
3	Hashmi Kohl Aswad bottle	Bought in a shop in Madrid, Spain Made in Pakistan	28 May 2019	Ingredients: Kohl powder, zinc oxide, amorphous black, blends of herbs Dose (both eyes) 1.4 mg corresponds to Pb 0.00%
4	Hashmi Kajal tube	Bought in a shop in Madrid, Spain Made in Pakistan	28 May 2019	Ingredients: Zinc oxide, waxes, processed carbon black, herbs, clarified butter, *Cinnamomum camphora* Dose (both eyes) 0.5 mg, Pb 0.00%
5	Khojati Mumtaz Herbal Kajal with almond oil	Bought in a shop in Manchester, UK Made in India	11 Sep 2019	Contents: Cow's glee (30.5 % w/w), Black iron oxide (8.0 % w/w), Waxy base (ad 100 % w/w) Tested in laboratory, free from lead
6	Khojati Mumtaz Delux Kajal (special quality)	Bought in a shop in Manchester, UK Made in India	11 Sep 2019	Contents: Coconut oil (31.3 w/w), Cow's ghee (18.0 % w/w), Sufoof-e-Syah (6.0 w/w), Bhimseni Kafoor (2.0 w/w), Roghan-e-Baid Anjeer (1.8 w/w), Sange Basari (0.4 w/w), Waxy base (ad 100 % w/w) Tested in laboratory, free from lead

7	Khojati Mumtaz Delux Kohl	Bought in a shop in Manchester, UK Made in India	11 Sep 2019	Contents: Gile Surkh (50.0 w/w), Sufoof-e-Syah (33.0 w/w), Sange-e- Basari (17.0 w/w) Soaked in 5% almond oil Tested in laboratory, free from lead
8	Natural kohl powder Black natural eyeliner No brand	Bought from eBay; delivered in Luxembourg, sent from Germany Made in Morocco	13 Oct 2019	No composition
9	Kohl Al-Sherifain[a] (2)	Bought from Amazon.de; delivered in Luxembourg, sent from Spain Origin India	12 Oct 2019	Free from lead Active ingredients: Sankh (42.5 %), Sufoof-E-Syah (42.5 %), Bhimseni Kafoor (15 %)
10	Kohl Al-Sherifain[a] (1)	Bought from Amazon.de; delivered in Luxembourg, sent from Spain Origin India	12 Oct 2019	Free from lead Active ingredients: Sankh (42.5 %), Sufoof-E-Syah (42.5 %), Bhimseni Kafoor (15 %)
11	Sheida. Kohl powder	Bought from Amazon.de; delivered in Luxembourg, sent from Germany Made in Turkey	12 Oct 2019	Ingredients: Talc, mica, nylon-12, ethyleneacrylic acid copolymer, isoestearyl neopentanoate, phenoxyethanol, caprylic glycol, sorbic acid
12	Intense kohl, crayon yeux No brand	Bought in a shop in Brussels, Belgium Origin unknown	30 Oct 2019	Ingredients: triethylhexanoin, cera carnauba, candeiilla cera, caprylic/capric triglyceride, polybutene, bis-diglyrecyl polyacyladipate-2, talc, cetyl palmitate, tocopheryl acetate, parfum, benyzl salycilate, buthylphenyl methylpropional, linalool

13	No label, no brand	Bought in a shop in Brussels, Belgium Origin unknown	30 Oct 2019	No composition
14	Al-Ameerah eye make-up	Bought in a shop in Brussels, Belgium Made in Pakistan	30 Oct 2019	No composition in English
15	Hatimi Eye-liner	Bought in a shop in Brussels, Belgium Made in India	30 Oct 2019	Ingredients: Carbon black, comphor, alum, menthol
16	Seeme Kajal	Bought in a shop in Brussels, Belgium Made in Pakistan	30 Oct 2019	No composition
17	Mumtaz Delux Surma (export quality)	Bought in a street market in Gaillard, France Made in India	14 Dec 2019	Contents: Ochre rouge 50.00%, carbone noire naturelle 33.00%, oxyde de zinc 17.00%. Imbibé d'huile d'amande à 5% (in French in the original)
18	Al-Asmad Alharmain	Bought in a shop in Geneva Made in IRP; address in Dubai	16 Dec 2019	Zam Zam & Rose water
19	Pure kohl Ithmid eyeliner powder Antimony Health Means Wealth	Bought from eBay; delivered in UK, sent from UK Origin: Yemen	31 December 2019	No composition

20	Kohl. No brand	Bought from eBay; delivered in UK, sent from UK Origin: Morocco?	31 December 2019	No text in English Text in eBay: Fair trade Moroccan kohl. Black eyeliner-hand carved wooden bottle and kajal
21	Kohl. No brand	Bought in eBay, delivered in Luxembourg, sent from Algeria Origin: Morocco?	31 December 2019	No composition Text in eBay: kohl Moroccan wooden bottle hand-made mascara surma eyes attractive eyeliner new
22	Surma stone	Bought from eBay; delivered in UK, sent from UK	31 December 2019	No composition Text in eBay: 100g surma Ithmid kohl pure stone
23	Surma stone	Bought from eBay; delivered in Luxembourg, sent from India Origin: India	31 December 2019	No composition (the stone arrived wrapped in a newspaper) Text in eBay: Surma stone antimony kohl stibine kajal 100 g natural eyeliner Hindu Muslim cool

Table 2. Elemental concentrations (mg kg^{-1}) in the kohl samples determined by XRF. Concentrations of other elements present are in table S2.

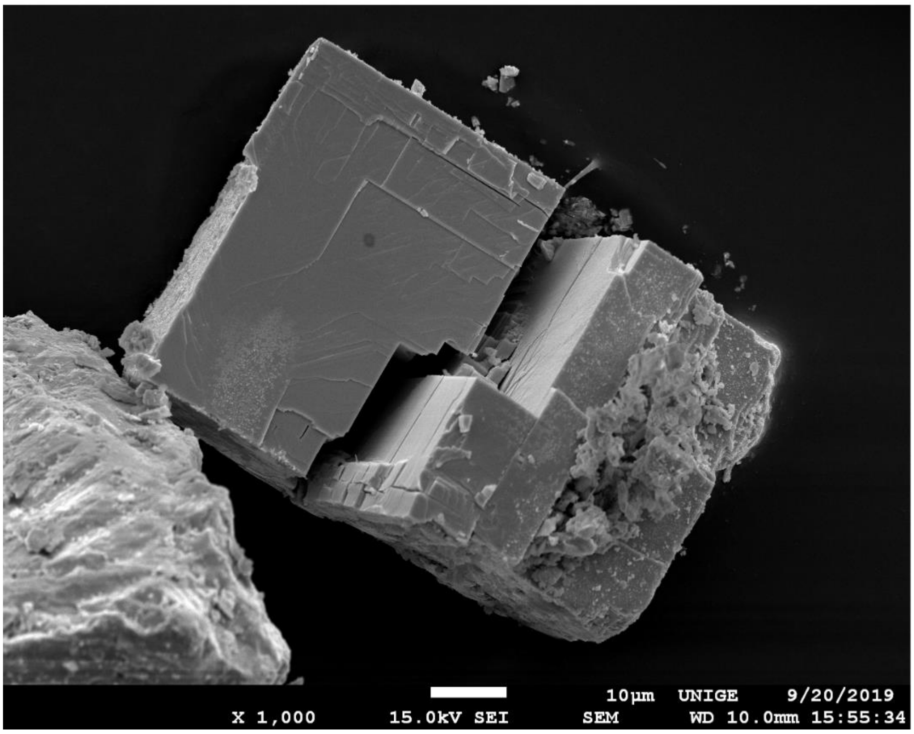
Sample	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Mn	Ni	Pb	Sb	Sn	Ti	Zn
1	987	11501	369	241		471	1838		766	576	444 507		344		2522
2		32 625	19.8		59	207	18 416	1213			112			943	37 994
3		1358	311	229		498	547		735	455	440 957	217	286		4273
4	294	435			64										380 827
5			17.2		79		121 861								
6		18 708			224	140	77 867	867			1431			7394	144 241
7			17.6				367				8				7730
8		5549				107					323			169	
9		44 426	14.5	134		190	12 934	560			39			668	34 892
10		66 367	17.3	236	60	255	15 072	872			36			1046	41 150
11		2017			303		371 485	7261	1098				370	20 796	2159
12		3653	18.4				34 201	11 606					222	44 918	
13	2648	2814	270	356		143	403	1191	777	448	441 466	217	236		122
14		165	17.9												
15	156 380	5245		268		178	6375		6905	1061	62				7502
16		276	17.4												
17		8298			241	213	133 247	1184	193		203			17 889	149 673
18	621	993	160	177		428	338		547	371	311 820	174	208		492
19	650	2348	275	311		710	995		762	637	467 632	149	315		7580
20		1448		0	983	184	354 929	536	3836	269	25 988			590	94
21		26 268				216	619	158 184			41795		155		180
22		10 267						1839			40 321				
23	1033	34 685			169	164	21 594	20987	1384	826	438 351			3650	6903

Table 3. Key morphological and chemical characteristics of the samples obtained by SEM-EDXS analysis. Complete information, including SEM pictures of all samples, is found in Table S3. All values are in molar percentages.

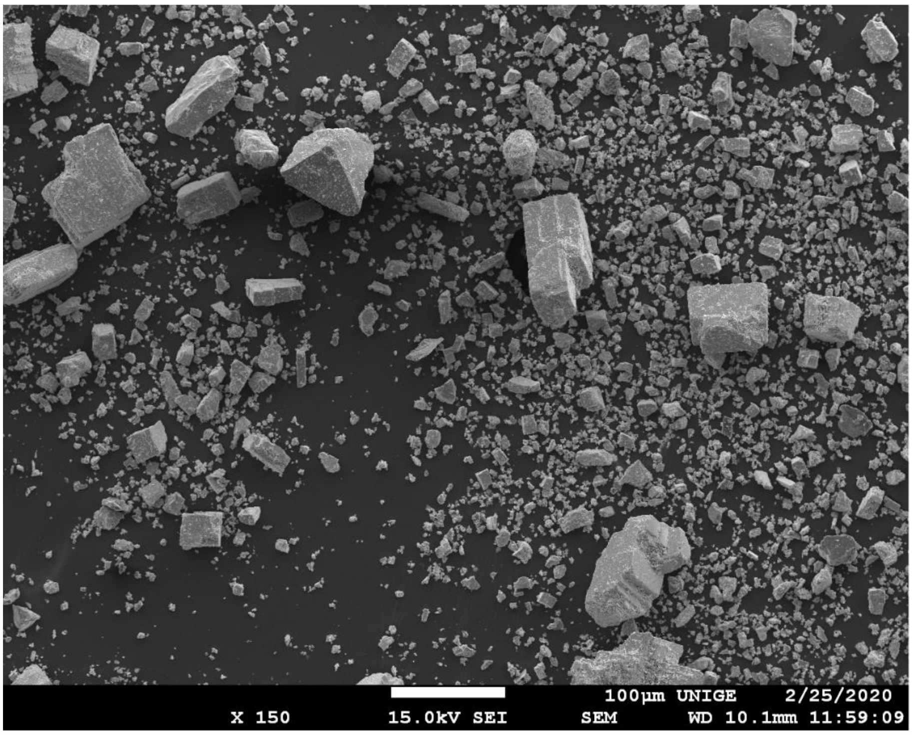
ID	Observations
1	Many size homogeneous cubes observed, with composition Pb:S = 60:40 Higher variability in the composition of particles in the agglomerates, ranging from Pb-S only particles to particles that, while containing a high % of Pb, also had Ca, Ti, Fe, Cu
2	Rather heterogeneous sample with probable presence of quartz and talc. Presence of Zn
3	Heterogeneous sample with, at least, three types of particles present: particles with Pb and S only (60:40 ratio), particles with C only and particles mostly containing Si and Mg (possibly talc)
4	C matrix that contains many small particles (size range: 150 to 800 nm with many at ~300 nm), detected in backscattered images. These particles contain Zn only by EDXS, possibly made of ZnO
5	C matrix with weak Fe signal. Analysis of backscattered images confirmed the presence of Fe nanoparticles. The presence of Fe was indicated by the producer (size range: 200 nm to 1 µm)
6	Rather heterogeneous sample with C only particles, particles rich in Si-Mg, Si-Al or Ca. Some contained Zn. Analysis of backscattered images confirmed the presence of nanoparticles containing high amounts of Zn, possibly ZnO (size range: 150 to 800 nm)
7	EDXS analysis showed either an entirely C matrix or C with a bit of Fe but Fe nanoparticles could not be found in backscattered images
8	All organic C
9	Two types of particles: Si-Mg and Zn-S. The Si-Mg particle has a similar composition as particles found in sample 10. Backscattered electron-imaging did not help to identify metal-rich particles
10	Organic matter with, at least, two types of minerals compounds, Si-Mg and Si-Na; the Si-Mg could be talc

11	On a substrate of aluminosilicates, abundant nanoparticles with Fe only (size range: 100-300 nm)
12	Organic matrix with aluminosilicates particles. Small particles containing Cu only were also spotted in backscattered images. Their sizes ranged from 1.5 to 5 μm
13	Many particles containing Pb and S only sitting on a C matrix. Pb:S ratio: 60:40
14	All organic C
15	Highly heterogeneous sample with different types of particles present (Si-Mg and pure organic C) including a lot of possible $BaSO_4$
16	All organic C
17	Heterogeneous sample. Results suggest the presence of particles are rich in Zn or Fe among others that contain Si, Al, Ti
18	Two different types of material. One consists of particles with Pb and S only (Pb:S ratio: 66:34) and the second type contains O and C only
19	All particles analysed contained Pb. Most had Pb and S only ((Pb:S ratio: 69:31) but one was 100% Pb, probably and Pb oxide None contained Sb, as said by the seller
20	Three types of particles detected by EDXS: one formed by organic C only, one 100% Fe and one with Pb and S, ratio 66:34
21	Two types of particles detected by EDXS: one formed by organic C and one with Pb and S, with a mean ratio 66:34
22	It is a compound of Pb and S, ratio 69:31
23	Not studied by SEM-EDXS

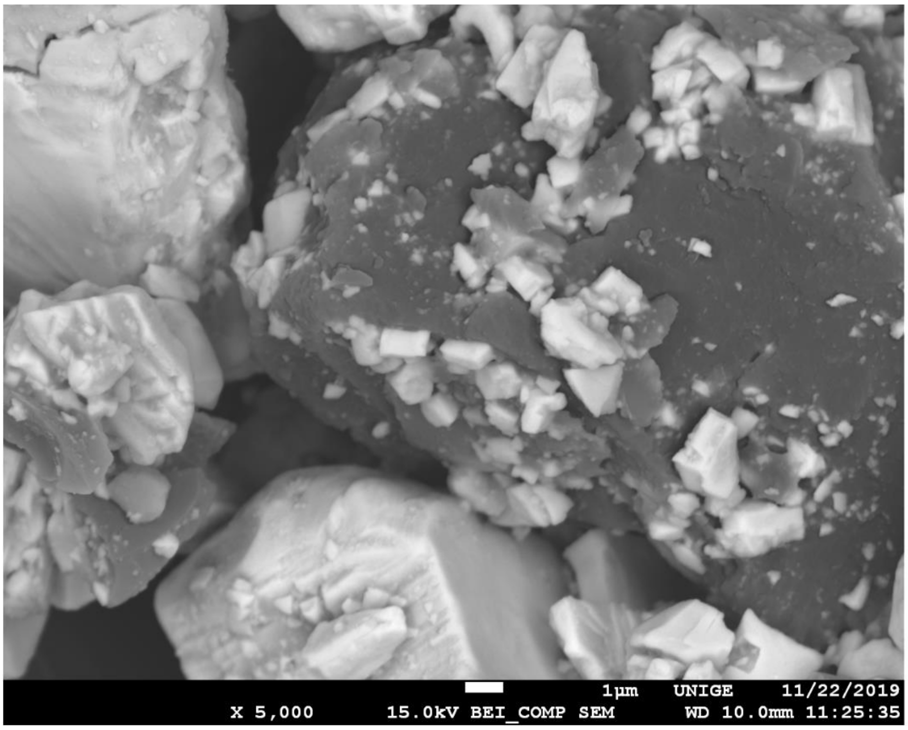
Figure 1. Pb-S compounds found in different samples: (a) #1, (b) #19, (c) #13, (d) #3, (e) #18. Compounds are revealed as isolated minerals of well-defined shape, as in (a), (b) and (e), or embedded in organic matrices, as in (c) and (d). Note that (c) is a backscattered electron image. Size is indicated at the bottom of the pictures.

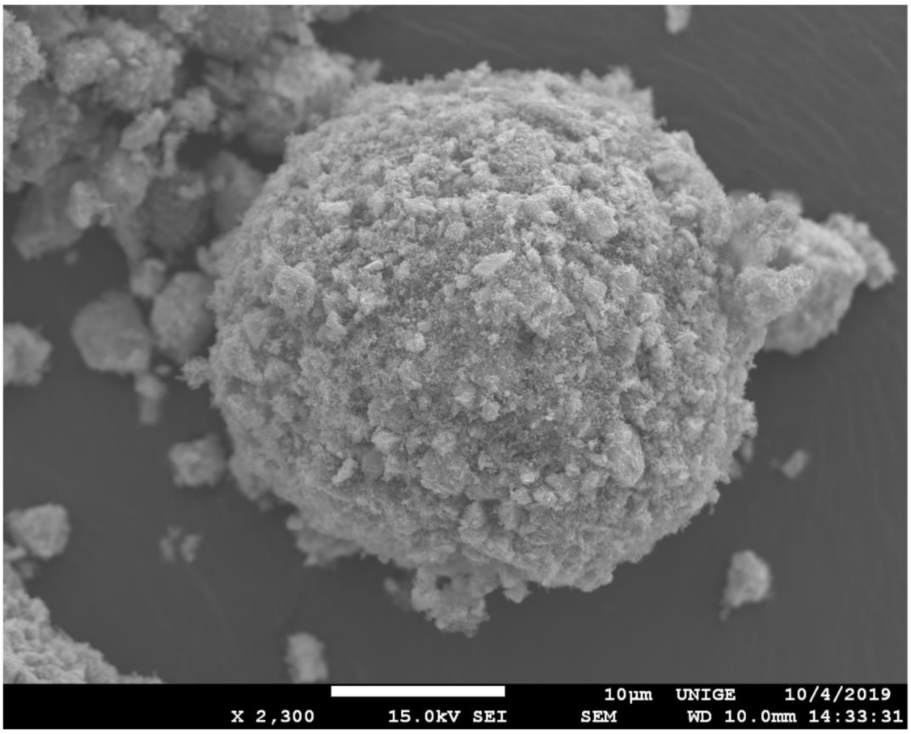


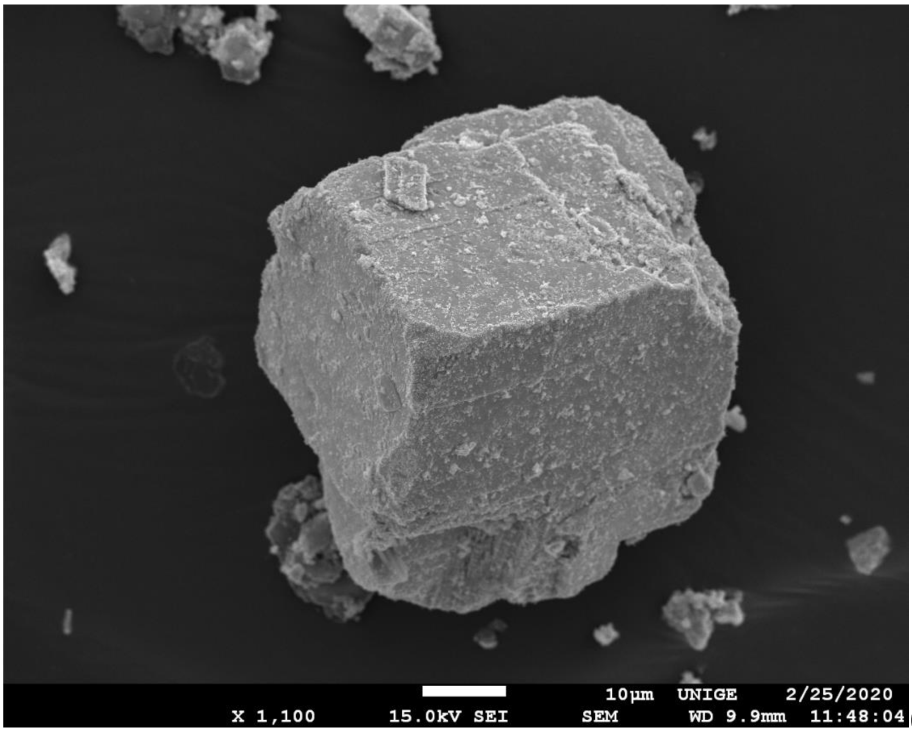
(a)



(b)


1µm UNIGE 11/22/2019
X 5,000 15.0kV BEI_COMP SEM WD 10.0mm 11:25:35
(c)

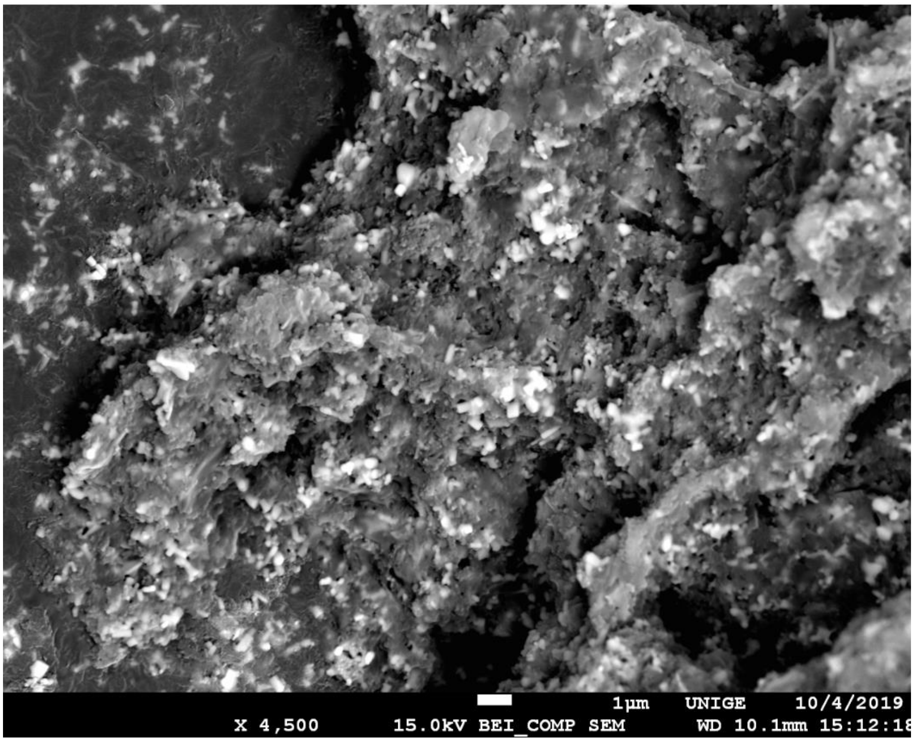

10µm UNIGE 10/4/2019
X 2,300 15.0kV SEI SEM WD 10.0mm 14:33:31
(d)

349 

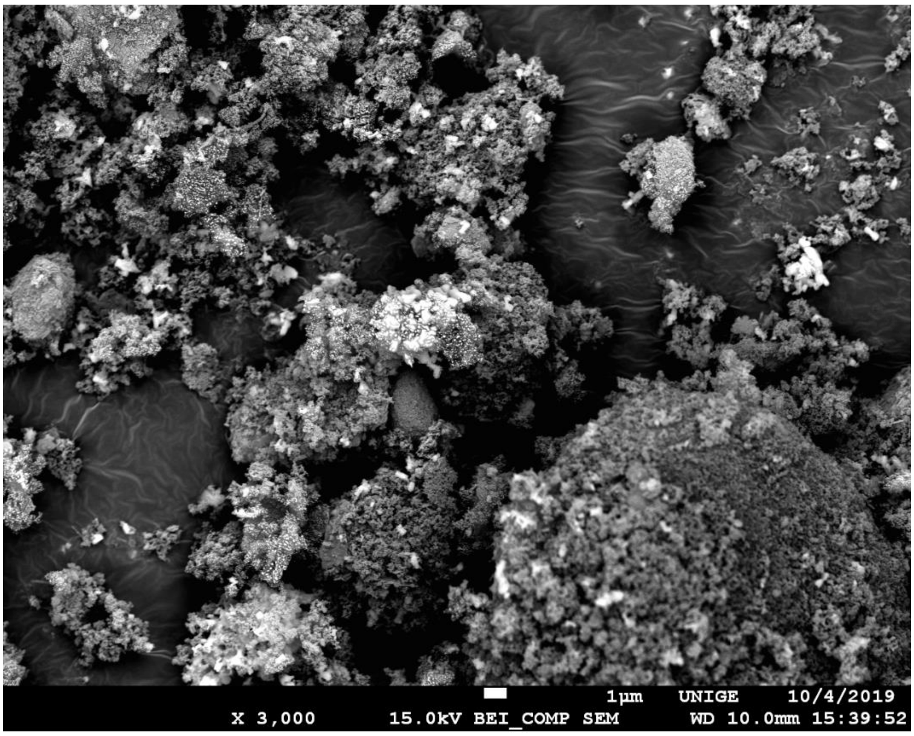
(e)

350

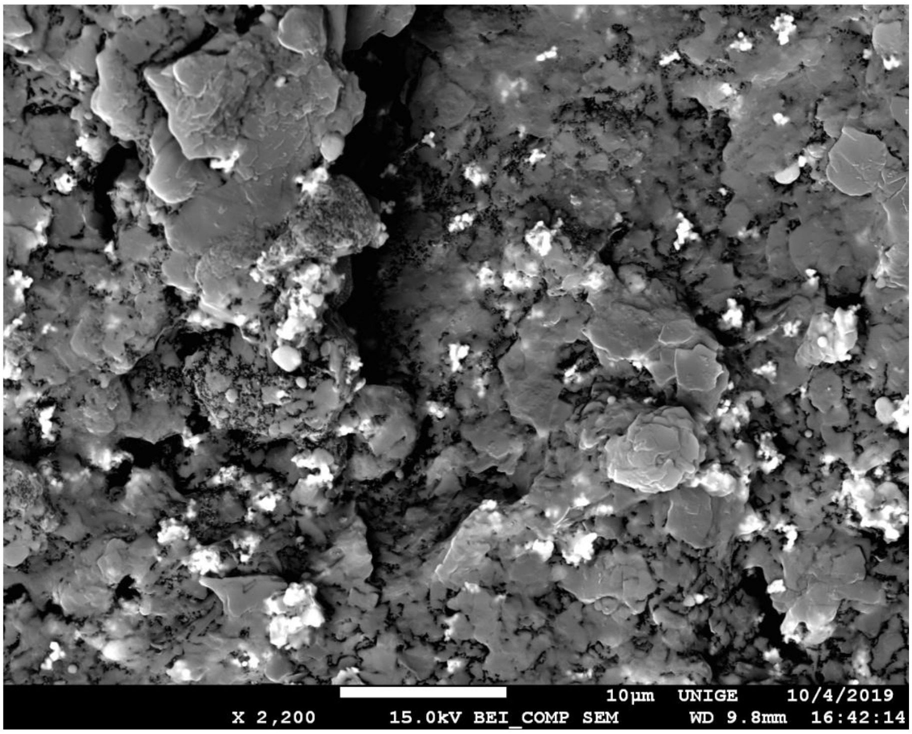
Figure 2. Backscattered electron images showing, in white against the darker surrounding material, (a) Zn nanoparticles in sample # 4, (b) Zn nanoparticles in sample # 6 and (c) Fe nanoparticles in sample # 5.



(a)



(b)



(c)