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Detection of metallic iron in urban dust by magnetic methods and microscopic observations

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Abstract

A thermomagnetic study was performed to identify the magnetic mineralogy of urban dust (indoor dust, outdoor dust, street dust, and dust from cabin air cars filters) collected from different environments. Temperature dependence of magnetic susceptibility κ(T) and induced magnetization M(T) were measured in the range of 30–700 °C and 30–800 °C, respectively. The presence of a "tail" in the heating curve of κ(T) between 600 °C and 700 °C is very often interpreted in the literature as evidence for the presence of hematite. However, the thermomagnetic curve of M(T) measured in the wider temperature range of up to 800 °C revealed that the Curie temperature of ~760 °C is typical of metallic iron. The presence of Fe-rich elongated shaving-like magnetic particles was confirmed by scanning electron microscopy observations. In various types of urban dust, the presence of metallic Fe can be due to traffic-related pollution as the concentration of elemental iron correlates with the key heavy metals Cu, Pb, Ba, Mn, Cr, and Zn, emitted by motor vehicles.

Keywords: Magnetic methods, Anthropogenic magnetic particles, Metallic iron, Traffic related heavy metals

1. Introduction

The use of magnetic methods to assess the levels of heavy metals pollution arises from the fact that both urban and industrial dust contains magnetic particles exhibiting

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ferromagnetic properties. Anthropogenic magnetic particles (AMPs) present in dust are associated with heavy metals and toxic trace elements; thus, the magnetic parameters such as magnetic susceptibility and magnetization, which are proportional to the concentration of AMPs, can be used to approximate the level of heavy metals pollution. However, recognizing the magnetic mineralogy of AMPs is required as it significantly affects the magnetic susceptibility.

A literature review (Muxworthy et al., 2002; Bućko et al., 2009; Magiera et al., 2011) indicates that AMPs consist mainly of iron in the form of oxides, i.e., magnetite, maghemite, and hematite. Our previous research (Górka-Kostrubiec et al., 2015, 2017; Szczepaniak-Wnuk & Górka-Kostrubiec 2016) of various types of urban dust (indoor, outdoor, and street dust) has shown that the magnetic fraction contains elongated shaving-like particles mainly composed of metallic iron. One of the methods of identifying the magnetic composition of AMPs is by measuring the temperature dependence of magnetic susceptibility (κ(T) curve), where a prominent strong decrease at the Curie temperature (T_C) is related to the magnetic transition of the ordered ferromagnetic state to the paramagnetic state. The Curie temperature is characteristic for each ferromagnetic mineral and can be used for their identification. In many cases, it is difficult to estimate the T_C for iron oxides because of chemical or crystallographic transformations occurring at high temperatures (Hanesch et al., 2016). This is the key problem observed in urban dust and it manifests itself as a substantial decrease of κ during heating at temperatures ranging from 600 °C to 700 °C, the so-called "tail" on the heating curve of κ(T). Current literature has various interpretations of the "tail" such as the presence of hematite, which is probably created during the partial oxidation of initial magnetite (Yang et al., 2011; Zhu et al., 2013; Jordanova et al., 2014; Bourliva et al., 2016) or as the presence of a phase with a higher Curie temperature like metallic iron or iron-based alloys (Górka-Kostrubiec et al., 2015, 2017; Szczepaniak-Wnuk & Górka-Kostrubiec 2016; Jeleńska et al., 2017). Resolving this issue is very important as the mixture of magnetite with metallic Fe or the mixture of magnetite with the same amount of hematite will affect magnetic susceptibility, thereby influencing the real level of heavy metal pollution.

The aim of the study is to prove that metallic iron is responsible for the substantial decrease of κ during heating from 600 °C-700 °C. For this purpose, we studied different types of urban dust (indoor dust, outdoor dust, street dust, and dust from cabin air filters of cars) collected using various methods to test whether or not metallic iron is commonly present in a strongly urbanized environment and is related to traffic pollution.

2. Methods and measurements

This study focussed the properties of different types of dust - indoor dust, outdoor dust, street dust, and dust from cabin air cars filters. For the interpretation of results, we have used the indoor dust sample collected from the floor of office spaces located in Warsaw, Poland. A detailed description of the sampling procedure for the collection and preparation of indoor dust can be found in previous works, e.g., Jeleńska et al. (2017).

Magnetic susceptibility describes the ability of materials to change magnetization when influenced by an external magnetic field and depends on the concentration of magnetic particles, their mineralogy, and grain-size distribution. In environmental studies, so-called mass magnetic susceptibility (χ) is most commonly used and it was measured using a MFK1-FA Kappabridge (AGICO, Czech Republic).

The temperature dependence of magnetic susceptibility, i.e., the curve of κ(T), was measured with the Kappabridge (KLY-3, AGICO) coupled with a CS-3 furnace operating at 20–700 °C. The heating and cooling curves of κ(T) were obtained in air, with a magnetic field of 300 A/m and a frequency of 875 Hz, and a heating and cooling rate of 11°C per minute. The temperature dependence of induced magnetization, i.e., the curve of M(T), was measured with an Advanced Variable Field Translation Balance (AVFTB, Petersen Instruments, Germany) with an applied magnetic field of 500 mT (≈400 kA/m). The heating and cooling M(T) curves were obtained at 35 °C–800 °C in air with a heating and cooling rate of 20 °C per minute. In both experiments, the sample mass was about 150–180*10^{-6} kg. The Curie temperatures were estimated from the inflection point of heating and cooling curves of κ(T) and M(T) using the second derivative method.

The total concentration of 14 elements including Cu, Cd, Co, Cr, Fe, Mn, Ni, Pb, Al, Ti, As, Ba, Sr, and Zn were estimated by subjecting the dust to microwave digestion (Milestone UltraWAVE, 1500W) in diluted HNO_3 and applying linear heating up to 270 °C at the rate of 12.5 °C per min., heating at 270 °C for 15 min, and then cooling to room temperature. The extract was measured by inductively coupled plasma- mass spectrometer (ICP-MS, ELAN 6100DRC, PerkinElmer). The elemental concentrations were determined in mg/kg of dried mass.

Morphology, shape, and chemical composition of the magnetic extract (separated using a hand magnet) were characterized by scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectrometer (EDS).

3. Results and discussion

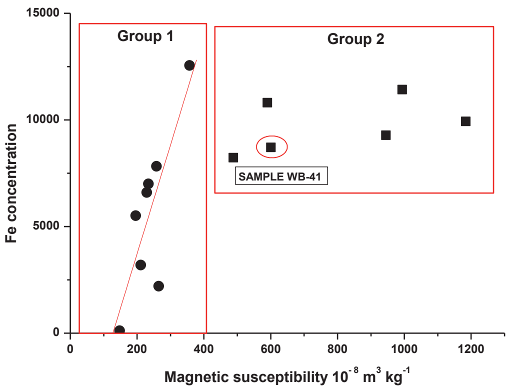

Fig. 1. Dependence of magnetic susceptibility on the concentration of elemental iron (in mg/kg)

Two groups of data can be recognized on Figure 1, which shows the dependence of magnetic susceptibility on the concentration of elemental iron (see Fig. 1). In group 1, the Fe concentration is in line with the increase in magnetic susceptibility. This may probably be due to the presence of iron in the form of magnetite and other paramagnetic compounds which adds almost proportionally to the magnetic susceptibility. In group 2, the high iron concentration significantly increases the magnetic susceptibility (Fig. 1), thus suggesting the presence of a strong magnetic component such as metallic iron. The latter hypothesis can be verified by performing two experiments – measurement of κ(T) curve in the range of

20–700 °C (Fig. 2a) for group 2 sample and the measurement of M(T) curve over the wider range of 20–800 °C (Fig. 2b). Such experiments can help to correctly interpret the "tail" visible on the heating curve κ(T) in the range of 600–700 °C.

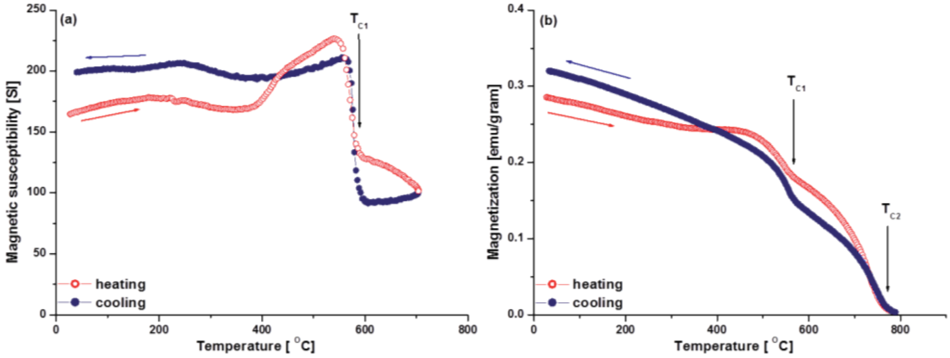

Fig. 2. Temperature dependence of magnetic susceptibility κ(T) curve (a) and induced magnetization M(T) curve (b). T_{C1} and T_{C2}, the Curie temperatures for magnetite and metallic iron, are marked, respectively

In Figure 2, the curves of both κ(T) and M(T) clearly showed the Curie temperature, T_{C1}, at ~585 °C, confirming the presence of magnetite in a dominant magnetic phase. For κ(T), heating at 600 °C to 700 °C causes rapid decrease in temperature until it reaches the T_C of magnetite. Regarding the M(T) curve, the induced magnetization continues to decrease above 600 °C with increasing temperature and, finally, the second Curie temperature T_{C2} is observed at ~760 °C. The temperature range of the second magnetic transition can be attributed to metallic iron or the iron-based alloys, which confirms our hypothesis that the "tail" on the κ(T) curves are due to the presence of high-temperature metallic iron-bearing phases. Moreover, the magnetic susceptibility of hematite, α-Fe_2O_3, is almost one order of magnitude lower than that of magnetite and almost two orders lower than that of pure iron, and thus, the presence of hematite cannot explain the relation visible in Figure 1. In group 2 samples, the relatively high concentration of iron is associated with high magnetic susceptibility.

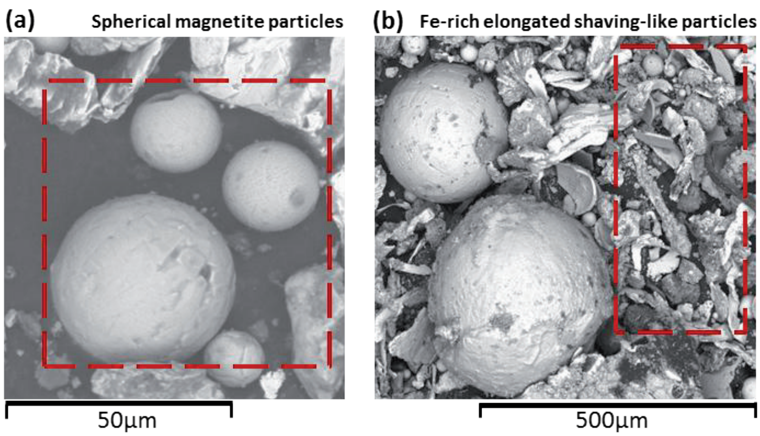

Fig. 3. Scanning electron microscopy observations (SEM) for indoor dust WB-41 selected from the samples of group 2 in Fig. 1.

SEM observations with EDS analysis were conducted to assess the approximate size and composition of magnetic particles. The images revealed spherical magnetite particles differing in surface morphology and with diameter ranging from 300 μm to less than 20 μm (Fig. 3a). Irregularly shaped particles not smaller than 10 μm and some shaving-like elongated particles (100–500 μm across; Fig. 3b) were also observed. The EDS analysis reveals that the shaving-like particles contain iron but no oxygen, i.e. they are metallic iron. The concentration of heavy metals was used to calculate the correlation between Fe concentration and traffic-related heavy metals (Fig. 4). Correlation coefficients ranged from 0.4 to 0.75 for Cr, Pb, Zn, and Cu, whereas they were $R > 0.8$ for Ba and Mn. We have confirmed that the magnetic fraction of dust contains magnetite and metallic iron as a result of processes related to vehicular traffic. Moreover, in various types of urban dusts, the presence of metallic Fe can be diagnostic of traffic-related pollution as the concentration of elemental iron is correlated with heavy metals, i.e., Cu, Pb, Mn, Cr, and Zn (Fig. 4) originating mainly from the abrasion and corrosion processes of moving vehicles.

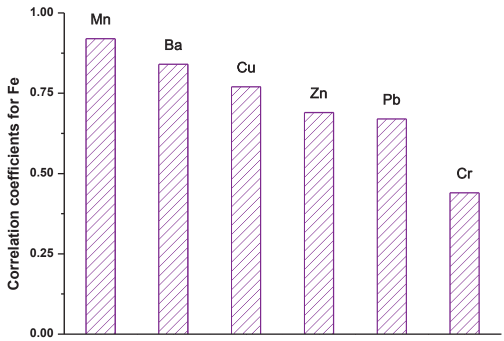

Fig. 4. Correlation coefficients of Fe concentration with traffic-related heavy metals Mn, Ba, Cu, Zn, Pb and Cr

4. Conclusions

The characteristic "tail" on the κ(T) curve should be interpreted as the presence of metallic iron, recognized by estimating the Curie temperature T_C ~760 °C on the M(T) curves and confirmed by SEM observations.

Metallic iron present in various types of dust – indoor dust, outdoor dust, street dust, and dust from cabin car filters – can be considered as an indicator of traffic–related pollution. It was confirmed by the relatively strong correlations of Fe concentration with traffic-related pollution of heavy metals such as Cu, Pb, Mn, Cr, Ba and Zn.

Magnetic methods offer a relatively rapid, inexpensive, noninvasive, and sensitive tool for evaluation of traffic–related pollution in environmental monitoring programs.

5. Acknowledgements

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