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CHARACTERISATION OF URBAN AIRBORNE PARTICULATE USING AUTOMATED MINERALOGICAL ANALYSIS

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ХАРАКТЕРИСТИКА ЧАСТИЦ ГОРОДСКИХ АТМОСФЕРНЫХ ВЫПАДЕНИЙ С ИСПОЛЬЗОВАНИЕМ АВТОМАТИЗИРОВАННОГО МИНЕРАЛОГИЧЕСКОГО АНАЛИЗА

In 2013, Williamson, Rollinson and Pirrie published the first automated mineralogical/phase assessment of urban airborne PM₁₀ and a new method for determining particle surface mineralogy (PSM) which is a major control on PM toxicity in the lung (Williamson et al., 2013). Particulate was analysed on a TEOM filter (Aug.–Sept. 2006 collection) using a QEMSCAN® automated mineralogical analysis system. A total of 381981 points of analysis were undertaken on 14525 particles in the size ranges PM₁₀₋₄, PM_{4-2.5} and PM_{2.5-0.8}. The method had a detection limit for individual mineral components of 0.05 ppm (by area). PM₁₀₋₄ made up 94 % and 79 % of the mineral mass and surface area, respectively, whilst PM_{2.5-0.8} contained 2 orders of magnitude more particles than PM₁₀₋₄ and PM_{4-2.5}. PSM of the PM₁₀ was dominated by gypsum (36 %), plagioclase (16 %), Na sulphates (8 %) and Fe-S-O phases (8 %) in the PM_{10-2.5}, which may be important in explaining the toxicity of the coarse fraction.

Figures 2. Table 1. References 8.

Key words: urban particle, automated mineralogical analysis, toxicity.

В 2013 году Вильямсон, Роллинсон и Пирри опубликовали первые данные по автоматизированной минералогической оценке фаз городских атмосферных частиц фракции менее 10 микрон (PM₁₀) и данные по новому методу для определения поверхностной минералогии частиц (particle surface mineralogy – PSM), который является основой контроля токсичности частиц в легких (Williamson et al., 2013). Микрочастицы были проанализированы на фильтре ТЕОМ (коллекция августа–сентября 2006 г.) с использованием автоматизированной минералогической системы QEMSCAN®. В общей сложности были проанализированы 381981 участков анализа на 14525 частицах в диапазонах размерности частиц PM₁₀₋₄, PM_{4-2.5} и PM_{2.5-0.8}. Предел обнаружения метода составил для отдельных минеральных компонентов 0.05 г/т (для локальных областей анализа). Частицы PM₁₀₋₄ составили 94 % и 79 % минеральной массы и площади поверхности соответственно, в то же время, частиц PM_{2.5-0.8} содержалось на 2 порядка больше, чем PM₁₀₋₄ и PM_{4-2.5}. Поверхностная минералогия частиц PM₁₀ характеризовалась преобладанием гипса (36 %), плагиоклаза (16 %), сульфатов натрия (8 %) и Fe-S-O фазы (8 %) во фракции PM_{10-2.5}, которая может быть важной в объяснении токсичности «грубодисперсной» части атмосферной уличной пыли.

Илл. 2. Табл. 1. Библ. 8.

Ключевые слова: городские атмосферные частицы, автоматизированный минералогический анализ, токсичность.

1. Introduction

The World Health Organization has estimated that airborne particulate contributes to over 2 million deaths per year worldwide (WHO, 2011). Particularly worrying is the fine fraction, with aerodynamic diameters $< 2.5 \mu\text{m}$ ($\text{PM}_{2.5}$), which can penetrate into the alveolar regions of the lung (QUARG, 1996). However, there is also evidence that the coarse fraction ($\text{PM}_{10-2.5}$), which mainly deposits in the upper airways, can also adversely impact on human health (Diociaiuti et al., 2001). Despite numerous studies, the exact causes of PM toxicity remain poorly understood, mainly because of the difficulty in characterizing the physical and chemical properties of complex mixed dusts. Factors affecting toxicity may include particle shape, solubility, speciation of contained toxic substances and surface properties, all of which are at least partly governed by mineralogy. Of particular significance is particle surface mineralogy (PSM) as this largely determines the nature and extent of potentially deleterious reactions within lung.

In general, $\text{PM}_{2.5}$ is mainly composed of organic and elemental carbon, and sulphate and nitrate-based compounds, largely produced from combustion processes and atmospheric gas condensation and gas to particle conversion (Gieré, Querol, 2010). The coarse fraction is largely formed by mechanical processes during industrial and construction activities, re-suspension of soil and street particles, and from sea spray, and may often contain pollen, fungal spores and plant and animal fragments (Gieré, Querol, 2010).

The aims of Williamson et al. (2013) were to: 1) to demonstrate the potential of QEMSCAN® for the mineralogical analysis of PM_{10} , particularly PSM, and 2) to provide the first large (~15,000 particle) dataset on the mineralogical composition of urban PM_{10} .

2. Methodology

A full description of the methodology and limitations of the techniques used are given in Williamson et al. (2013), and are summarised below. The filter analysed was from a Tapered Element Oscillating Microbalance (TEOM, manufactured by Rupprecht & Patashnick) which is used by the London Air Quality Network and many other authorities throughout the world for the continuous measurement of ambient airborne PM_{10} and $\text{PM}_{2.5}$. However, the methodologies tested in this paper could, within reason, be applied to the analysis of any airborne particulate collection. The TEOM filter

analysed was for a PM_{10} collection from the Bexley - Thames Road South site (BX8) in East London, UK (start: 10/8/06, 10:30; end: 26/9/06, 12:15) kindly provided by the TEOM Filter Archive. The average PM_{10} concentration during the sampling period (i.e. for the filter analysed) was 23 mg/m^3 .

The TEOM filter cartridge was embedded in EPO-TEK® 301-2 epoxy resin at an angle of around 70° to the face of the block so that the surface could be ground down to reveal a cross section through the filter. The block was ground dry and then polished using Kemet water-free 1 mm diamond slurry (1-KDS1429) to limit dissolution of water soluble phases. For QEMSCAN® analysis, the surface of the polished block was carbon coated to a thickness of ~25 nm.

The sample was analysed in a QEMSCAN® 4300 automated mineral analysis system at the Camborne School of Mines, UK. This is capable of determining size, shape and mineral/phase composition for over 1000 particles per hour, for particles 1 to 10 μm in diameter and with a 1 mm measurement spacing (Pirrie et al., 2004). Imaging of an area of the sample surface ($12.000 \times 1.000 \text{ mm}$) was first carried out in backscattered electron (BSE) mode where brightness is proportional to average atomic number. ABSE threshold was set, calibrated using quartz and gold standards, to ensure the recognition of particles with a BSE grey scale above that of the resin block. Energy dispersive X-ray (EDS) analysis, as part of QEMSCAN®, was then carried out in a grid pattern (0.5 mm grid spacing) within all recognised particles, with a total of 1000 X-ray counts collected per analysis. 381981 points were analysed in 14525 identified particles over a data acquisition time of 9 h 54 min. The spatial «resolution» of the analyses (smallest particle identified) was 0.8 μm and the theoretical detection limit for individual minerals was around 0.05 ppm (by area). The data from each point of analysis was automatically compared with a database of mineral and non-crystalline phase spectra to identify the mineral/phase present. A mineral map, known as a Fieldscan image, of the sample surface was produced using the coordinates of the individual points of analysis (Fig. 1a).

A notable problem with any sort of EDS analysis is that minerals with the same (or very similar) chemistries cannot be differentiated. Mineral categories used in the data analysis (Williamson et al., 2013) therefore include several possible individual minerals: «Gypsum – may include other Ca sulphates; Quartz – quartz or boundary affect (see below); Na sulphates – any mineral with

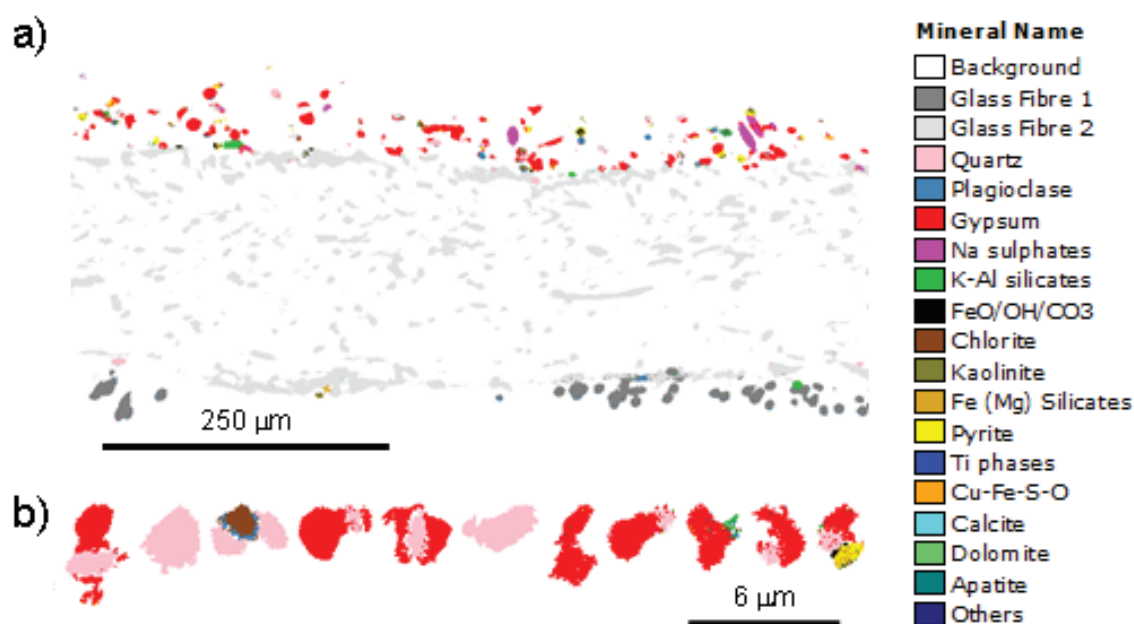


Fig. 1. a) QEMSCAN® 'Fieldskan' image showing mineral particles on the surface of the TEOM filter substrate; b) Higher magnification images of individual particles on the TEOM surface.

Рис. 1. a) QEMSCAN® изображение, демонстрирующее минеральные частицы на поверхности TEOM фильтра; b) Изображения отдельных частиц на поверхности TEOM фильтра с большим оптическим разрешением.

Na, S, O, ± Mg; Plagioclase – any mineral with Na, Al, Si, O to Ca, Al, Si, O (may include trace areas of the TEOM filter); K-Al-silicate – any mineral with K, Al, Si, O (e.g. K-feldspar, muscovite); Fe-S-O – any mineral with Fe, S, and possibly O (e.g. pyrite, melanterite, jarosite); Fe(Mg) silicates – any mineral with Si, Mg, Fe such as olivine or talc; Ti minerals – any mineral with Ti and O such as rutile, titanite, ilmenite and paint flakes; FeO/OH/CO₃ – Fe metal, oxides, hydroxides and carbonates (e.g. hematite, goethite, siderite); Calcite – any mineral consisting of Ca with or without C and O; Chlorite – may include tourmaline, vermiculite and other Fe, Al, Si and Fe, Mg, Al, Si minerals; Kaolinite – any mineral with Al and Si with low Fe and Mg; Cu-Fe-S-O – Cu-Fe sulphides or sulphates; Dolomite – any mineral with Ca and Mg with or without C and O; Apatite – any Ca phosphates; Other – any other mineral not included above».

For each particle analysed a mineral map was created from which the size/shape (area, perimeter length, axis lengths etc.) and mineral associations were derived. PSM was calculated from the number of pixels of different minerals in direct contact with 'background' (either filter substrate, carbonaceous material or resin mounding medium). Data for these parameters was output for the following health pertinent particle size ranges: PM₁₀₋₄, PM_{4-2.5} and PM_{2.5-0.8} (fine fraction), and from this the coarse fraction (PM_{10-2.5}).

3. Results

The presence of airborne particulate on the surface of the filter is clear from the image in Figure 1a, mainly being contained within a roughly 0.1 mm thick layer on the upper surface. The particles are widely spaced due to the likely presence of carbonaceous particles which are not distinguishable from the resin substrate. From the particle mineral maps in Figure 1b, most particles can be seen to be entirely or partially made up of gypsum, which often forms coatings on other minerals. With reference to Table 1, gypsum shows a clear association with Na sulphates, plagioclase, K-Al-silicates and Fe-S-O, and to a lesser extent chlorite and quartz. Other notable associations are between plagioclase and K-Al-silicates and chlorite, and between Fe-S-O and FeO/OH/CO₃.

Table Mineral associations matrix for different size classes (PM₁₀₋₄, PM_{4-2.5} and PM_{2.5-0.8}) showing number of pixels of each mineral in direct contact with other minerals. Mineral names along the top row are abbreviations of those in the first column. Taken from Williamson et al. (2013).

The total number of particles in the PM₁₀₋₄, PM_{4-2.5} and PM_{2.5-0.8} size fractions was found to vary widely, the PM₁₀₋₄ fraction containing 434 particles, the PM_{4-2.5} fraction only 199 particles and the PM_{2.5-0.8} fraction 13.891 particles (excluding quartz). The PSM of the PM₁₀ is

heavily dominated by the $PM_{10-2.5}$ fraction which forms 85 % compared with 6 % for the $PM_{4-2.5}$ and 16 % for $PM_{2.5-0.8}$ (Fig. 2). Of the total PSM of the PM_{10} (for all minerals), the $PM_{10-2.5}$ fraction contained 36 % gypsum, 16 % plagioclase, 8 % Na sulphates and 8 % Fe-S-O phases.

4. Discussion

Adverse health impacts related to PM_{10} are generally attributed to the fine ($PM_{2.5}$) or respirable (PM_4) fraction

due to its small size, relatively large surface area and higher number concentration in ambient air (QUARG, 1996), smaller particles being able to penetrate into the alveolar regions of the lung (EPAQS, 2001). The filter analysed contained roughly two orders of magnitude more particles in the fine than the coarse fraction. However, the fine fraction had a relatively lower PSM (Fig. 2) We propose that the high PSM for gypsum (36 %), plagioclase (16 %), Na sulphates (8 %) and Fe-S-O phases (8 %) in the coarse fraction, as a

Table

Mineral associations matrix for different size classes (PM_{10-4} , $PM_{4-2.5}$ and $PM_{2.5-0.8}$) showing number of pixels of each mineral in direct contact with other minerals. Mineral names along the top row are abbreviations of those in the first column. Taken from Williamson et al. (2013)

Таблица

Матрица минеральных ассоциаций для классов частиц различной размерности (PM_{10-4} , $PM_{4-2.5}$ и $PM_{2.5-0.8}$), демонстрирующая число пикселей каждого минерала в прямом контакте с другими минералами. Наименования минералов по верхнему ряду являются их сокращениями в первой колонке. Взято из публикации (Williamson et al., 2013)

PM_{10-4}	BG	Gy	Qz	NS	Pl	Kf	FS	FSi	TP	FO	Ca	Ch	Ka	CF	Do	Ap	Oth
Background		44636	4507	10908	21368	5557	9555	1981	643	3048	150	3256	448	262	35	0	218
Gypsum	44636		586	4110	5708	2825	8327	77	97	78	11	1857	28	441	42	38	107
Quartz	4507	586		0	21	8	19	1	0	97	0	15	0	0	0	0	0
Na sulphates	10908	4110	0		22	20	598	1	7	9	9	9	0	124	0	0	21
Plagioclase	21368	5708	21	22		2554	1046	162	20	28	55	1720	172	4	35	0	3
K-Al silicates	5557	2825	8	20	2554		1147	22	8	49	0	1732	441	7	0	0	20
Fe-S-O	9555	8327	19	598	1046	1147		2641	14	4620	12	2996	20	228	3	0	8
Fe(Mg)silicates	1981	77	1	1	162	22	2641		9	1003	0	791	0	1	0	0	7
Ti phases	643	97	0	7	20	8	14	9		4	0	4	0	0	0	0	12
Fe Ox/OH/CO ₃	3048	78	97	9	28	49	4620	1003	4		0	403	0	0	0	0	1
Calcite	150	11	0	9	55	0	12	0	0	0		0	0	0	1	0	0
Chlorite	3256	1857	15	9	1720	1732	2996	791	4	403	0		251	12	0	0	74
Kaolinite	448	28	0	0	172	441	20	0	0	0	0	251		0	0	0	0
Cu-Fe-S-O	262	441	0	124	4	7	228	1	0	0	0	12	0		0	0	9
Dolomite	35	42	0	0	35	0	3	0	0	0	1	0	0	0		0	0
Apatite	0	38	0	0	0	0	0	0	0	0	0	0	0	0	0		0
Others	218	107	0	21	3	20	8	7	12	1	0	74	0	9	0	0	
$PM_{4-2.5}$	BG	Gy	Qz	NS	Pl	Kf	FS	FSi	TP	FO	Ca	Ch	Ka	CF	Do	Ap	Oth
Background		4566	237	311	639	420	1197	46	87	249	1	210	71	9	19	5	7
Gypsum	4566		3	85	348	157	474	7	9	2	3	64	1	25	0	7	3
Quartz	237	3		0	0	0	3	0	0	4	0	1	0	0	0	0	0
Na sulphates	311	85	0		1	1	39	0	0	0	0	0	0	1	0	0	0
Plagioclase	639	348	0	1		123	55	4	20	5	0	59	25	2	25	0	0
K-Al silicates	420	157	0	1	123		41	0	12	3	0	59	20	0	0	0	2
Fe-S-O	1197	474	3	39	55	41		57	13	162	0	102	0	3	0	0	0
Fe(Mg)silicates	46	7	0	0	4	0	57		0	5	0	7	0	0	0	0	0
Ti phases	87	9	0	0	20	12	13	0		0	0	1	0	0	0	0	0
Fe Ox/OH/CO ₃	249	2	4	0	5	3	162	5	0		0	24	0	0	0	0	0
Calcite	1	3	0	0	0	0	0	0	0	0		0	0	0	0	0	0
Chlorite	210	64	1	0	59	59	102	7	1	24	0		5	0	0	0	0
Kaolinite	71	1	0	0	25	20	0	0	0	0	0	5		0	0	0	0
Cu-Fe-S-O	9	25	0	1	2	0	3	0	0	0	0	0	0		0	0	0
Dolomite	19	0	0	0	25	0	0	0	0	0	0	0	0	0		0	0
Apatite	5	7	0	0	0	0	0	0	0	0	0	0	0	0	0		0
Others	7	3	0	0	0	2	0	0	0	0	0	0	0	0	0	0	

Table continuation

$PM_{2.5-0.8}$	BG	Gy	Qz	NS	Pl	Kf	FS	FSi	TP	FO	Ca	Ch	Ka	CF	Do	Ap	Oth
Background		12327		806	1893	1565	2623	170	134	360	8	560	131	43	2	4	0
Gypsum	12327			37	160	79	248	0	4	1	2	47	1	3	0	0	0
Quartz																	
Na sulphates	806	37			0	1	19	0	0	0	0	0	0	1	0	0	0
Plagioclase	1893	160		0		36	16	1	1	2	0	26	1	0	0	0	0
K-Al silicates	1565	79		1	36		19	0	1	9	0	43	4	0	0	0	0
Fe-S-O	2623	248		19	16	19		42	2	50	0	58	0	3	0	0	0
Fe(Mg)silicates	170	0		0	1	0	42		0	4	0	3	0	0	0	0	0
Ti phases	134	4		0	1	1	2	0		0	0	0	0	0	0	0	0
Fe Ox/OH/CO ₃	360	1		0	2	9	50	4	0		0	18	0	0	0	0	0
Calcite	8	2		0	0	0	0	0	0	0		0	0	0	0	0	0
Chlorite	560	47		0	26	43	58	3	0	18	0		3	0	0	0	0
Kaolinite	131	1		0	1	4	0	0	0	0	0	3		0	0	0	0
Cu-Fe-S-O	43	3		1	0	0	3	0	0	0	0	0	10		0	0	0
Dolomite	2	0		0	0	0	0	0	0	0	0	0	0			0	0
Apatite	4	0		0	0	0	0	0	0	0	0	0	0	0			0
Others	0	0		0	0	0	0	0	0	0	0	0	0	0	0	0	

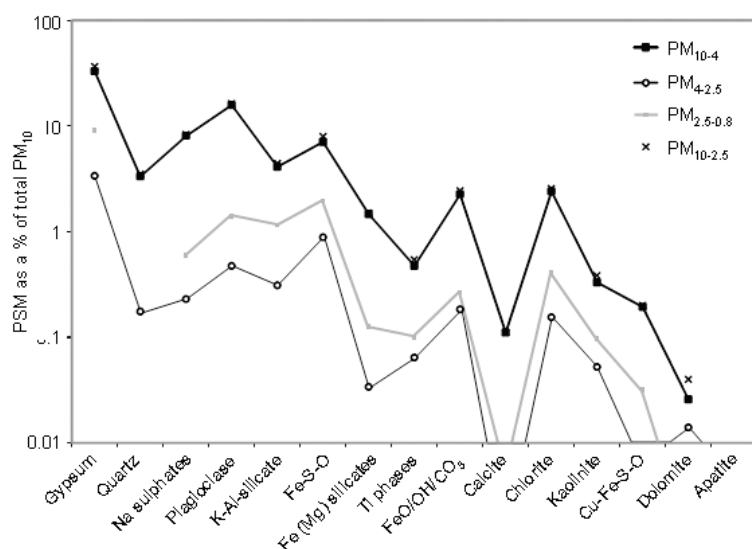


Fig. 2. Particle surface mineralogy (PSM) of each mineral in the size ranges PM_{10-4} , $PM_{4-2.5}$, $PM_{2.5-0.8}$ and $PM_{10-2.5}$, expressed as a % of the total mineral surface area of PM_{10} , i.e. all points in the graph add up to 100 %. Taken from Williamson et al. (2013).

Рис. 2. Поверхностная минералогия частиц (PSM) каждого минерала в диапазонах размерности PM_{10-4} , $PM_{4-2.5}$, $PM_{2.5-0.8}$ и $PM_{10-2.5}$, выраженная как процент полной площади поверхности минералов PM_{10} , т. е. все пункты в графе, составляют в целом 100 %. Взято из публикации (Williamson et al., 2013).

proportion of bulk PM_{10} , may explain why the coarse fraction can be, in certain respects, as toxic as the fine fraction. However, any attempt to prove this is likely to require much wider PSM analysis, for samples from different environments and showing different mineralogies and levels of toxicity, and comparisons with complementary chemical (organic and inorganic) and physical data.

The physicochemical characteristics of PM_{10} may give clues as to its source, which is an important factor in developing risk management strategies and for the identification of pollutants in forensics studies. The mineralogy of the PM_{10} in the case study herein was dominated by gypsum, either present as discrete particles or as coatings on other particles (see Fig. 1b). Gypsum in the urban environment is either likely to

originate from construction activities or from reactions between carbonate particles and sulfur dioxide or sulfuric acid (Xie et al., 2005). Quartz is amongst the most common silicates in the Earth's upper crust and could therefore have had a variety of origins. The K-Al silicates could include K-feldspar but also white mica (possibly sericite) which is a frequent alteration product of plagioclase and K-feldspar. Less common were Fe (Mg) silicates which may include the potentially toxic asbestiform amphibole and serpentine minerals such as crocidolite, amosite and chrysotile. The Fe-S-O category formed 2 % of PSM in the $PM_{2.5-0.8}$ (1020 particles) but shows low particle numbers (10) in the coarse fraction. Its mineral form and source is unclear although from its association with gypsum and FeO/OH/CO₃ (Table), it is thought

likely to be mostly present as sulphate, possibly the mineral melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$).

From the preliminary results of the Williamson et al. (2013) paper, it is clear that QEMSCAN[®] has significant potential to improve the characterisation and source identification of PM_{10} , particularly because of its excellent detection limits (0.05 ppm). The capabilities of this type of instrument are likely to improve greatly over time, being able to analyse smaller, possibly ultrafine, particles, and with more precise mineral/phase identification. The acquisition of large datasets for airborne particulate from different environments and experimental studies has great potential in epidemiological as well as toxicological research.

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