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Possibilities for analysis of selected nanometals in solid environmental samples

Anna Rabajczyk

Chair of Environmental Protection and Modelling, The Jan Kochanowski University in Kielce, ul. Świętokrzyska 15, 25 406 Kielce, Poland, email: anna.rabajczyk@ujk.edu.pl

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ABSTRACT

Nanotechnology is a field which is developing rapidly due to possibilities of applying nanoscale entities in most fields of human activity and everyday life. However, the presence of metal nanoparticles, including nano-oxides, free nanometals, in all fields of human economy and activity causes the volume of nanocompounds emitted to the biosphere to increase regularly. This is the reason for their gradual build-up in individual components of the environment, including soil and bottom sediments. Nanometals, as materials diversified in terms of chemical properties, require availability of analytical procedures which enable acquisition of reliable information on the presence, volume and physicochemical properties of nanometals. Traditional methods of environmental protection, as far as sample collection, processing and the analysis are concerned, must be adapted to the nanometals emitted into the environment. It must be added that, due to the wide range of nanometals, their selective determination constitutes a major challenge. The challenge is further aggravated by shortage of standard analytical procedures as well as reference substances necessary to ensure adequate control levels and the quality of analytical results. At each study level, these difficulties can be overcome by comparing the results of determinations obtained with a variety of analytical methods and techniques (such as XRD, SEM, FT-IR, UV–vis, NanoSight or ICP-MS-TOF). This kind of procedure enables assessment of possibilities for application of these techniques to standard determinations.

Keywords: Solid environmental samples; Nanometals; Analytical techniques

1. Introduction

The technology of entities whose dimensions range from a few to several tens of nanometres, that is nanotechnology, has a wide range of applications in the fields of chemistry, biology, medicine, engineering, information technology, etc. Due to population growth, limited resources as well as newly arising diseases and threats, nanotechnology is viewed as a major factor in economic and industrial development. Every year, the use of substances such as nanometals increases rapidly in fields such as biomedicine, pharmaceuticals, cosmetics, electronics, energy and environmental protection (Table 1), as evidenced by the fact that the global market for nanomaterials is estimated at 11 m tonnes per year, with a market

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Table 1
Examples of metal nanocompounds and their uses in various industries and in households

Industry	Nanometal forms	Examples	Application	Ref.
Cosmetic	Nanoparticles	Ag	Toothpaste, mouthwash, anti-dandruff shampoos, lotions	[3]
	Nanocolloids	ZnO, Au	Body lotions, moisturising oils	[3]
	Nanometal or metalloid oxides	ZnO	Sunscreen creams	[3]
	Dioxide nanometals	TiO_2, Fe_2O_3, Cr_2O_3	Sunscreen creams, powders, sun creams, lipsticks, eye shadows, nail polish, mascara	[3,4]
Pharmaceutical and Medicine	Nanoparticles	Ag, Cu, Au, Fe_3O_4/Au	Drug carriers, surgical sutures, bandages, wound and burn disinfectants, dressing materials antibacterial coating, surgical instruments and dialysis devices	[5–8]
	Nanocolloids	Ag, Au, Cu, Ag on different carriers (such as silica, polymer)	Fluids and disinfectants	[8,9]
	Nanometal or metalloid oxides	ZnO	Dentin-regenerating toothpaste	[3]
	Dioxide nanometals	TiO_2, SnO_2	Antibacterial catheters, drug carriers, implants	[3,10]
Textile	Nanoparticles	Ag, Au, Cu, SiO_2 (hfl)	Clothing, underwear, sheets, tablecloths, towels, mattresses	[11]
	Nanocolloids	Cu, CuO	Cotton production	[12,13]
	Nanometal or metalloid oxides	CuO	Antibacterial fabrics	[14]
Agri-food	Nanoparticles	Ag	Perishables, refrigeration components	[15–17]
	Nanocolloids	Ag, Cu, Ag/SiO_2	Fruit and vegetable sprays, equipment and installation decontaminants	[15–17]
	Dioxide nanometals	TiO_2	Food packaging foils	[15–17]
Paper and wood	Nanocolloids	Ag, Cu, Ag/SiO_2, SiO_2 (hfb)	Production hall disinfectants wood, paper and cardboard preservatives	[18,19]
Environment protecting	Nanocolloids	Ag, Cu, Au, nZVI, Cu-TiO_2/SBA15, TiO_2, CMC-nZVI	Water and wastewater treatment, recultivation, membrane, filters	[20–24]
Automotive and Transportation	Alloys	Zn–Mg–Al	Biofuel catalysts	[25]
	Nanoparticles	Ag, Cu, SiO_2 (hfl)	Filters, air conditioning, cloth and filter materials, upholstery, cables	[26–28]
	Nanocomposites	Al–SiC, Al–Mg–Si	Car, train and plane equipment components	[29,30]
Electronics, optoelectronics	Nanoparticles	ZnSe, Au, Al/CuO_x, Fe_3O_4/Au, oxide of: Sn, Ce, Co, Fe, Ni, Au, Ag, Cu	Transistor, detector, sensor and electroreduction components	[31–33]
Construction	Nanoparticles	Ag, Ag/SiO_2, Cu/Al_2O_3, Al-oleic acid	Windows and doors, building and sanitary ceramics, plaster, plasterboard panels, tiles, weight, putty, paint, grout, mortar, protective preparations, self-cleaning glass windows, solar collectors	[34–37]
Households	Nanoparticles	Ag, Cu, SiO_2 (hfl)	Washers, carpets, upholstered furniture, curtains, drapes, carpets, kitchen appliance antibacterial coating	[35,38–40]
	Nanocolloids	Ag, Cu, TiO_2	Surfactants, detergents	[41]
	Nanometal or metalloid oxides	ZnO	Kitchen appliance antifungal coating	[35,42]

Note: SBA-1—mesoporous silica nanoparticles named Santa Barbara Amorphous; hfl—hydrophilic; hfb—hydrophobic; nZVI—zerovalent iron; CMC—carboxymethyl cellulose.

value of €20bn [1]. In 2009, the Woodrow Wilson International Center for Scholars' Project on Emerging Nanotechnologies (Wilson Center) identified a list of more than 1,000 nano-enabled products currently on the market, reflecting a 379% increase since this list was first compiled in 2006 [2].

Yet new products, processes and materials based on nanosubstances carry the risk of nanosubstance emissions during the manufacturing process, product use and deposition. The fates and behaviour of these pollutants together with their metabolites and waste products may be potentially harmful to the environment and to humans [43–46]. This is why more and more frequently nanotechnology becomes the subject of discussion in the context of safety and risks. Much attention is paid to defining the toxicity of nanostructures in relation to various groups of organisms, including bacteria, protozoa, macrophytes, mice and rats [47–50]. The chief document which regulates the process of manufacturing, marketing authorisations and uses of various substances is the Regulation No. 1907/2006 of the European Parliament and of the Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH**)** (OJ L 396/1 30.12.2006). The REACH also pertains to nanomaterials on condition that a thorough analysis of the properties and threats of a particular substance is made. In the case of an increased potential risk carried by nanomaterials resulting, for example, from their cancerogenicity, mutagenicity and toxicity, it is obligatory to obtain special manufacturing and marketing authorisations [51–53]. Moreover, Directive 89/391/EEC (OJ L 183, 29.06.1989), which regulates employer obligations concerning provisions for employee health and safety, pertains to nanomaterials at each level of manufacturing and distribution, regardless of the means and technologies used in order to obtain them.

In legal terms, all products, nanomaterials included, require risk assessment and approval of control mechanisms. For environmental protection and its requirements, as far as nanomaterials are concerned, significant are also Directive 2008/1/EC of the European Parliament and of the Council of 15 January 2008 (OJ L 24, 29.1.2008), concerning Integrated Pollution Prevention and Control, Directive 2012/18/EU concerning the management of hazards and serious breakdowns with participation of dangerous substances (OJ L 197/1, 24.7.2012), Water Framework Directive (OJ L 327, 22.12. 2000) and the document on "Regulatory aspects of nanomaterials" (2008/2208 (INI)). The latter pertains to the possibility of controlling nanoscale operations and products, with a focus on "testing protocols" and "risk assessment methods."

The highest risk related to nanotechnology is the lack of control thereof. In particular, there are no technical means for monitoring, for example, the natural environment for the presence and influence of nanoparticles and nanomaterials. There exist no regulations, either at local or international levels, which would standardise the level of such control. Hence, for further operation of nanoscience and nanotechnology in life and economy, the development of adequate measurement tools is of paramount importance.

2. The source of origin of nanometals in selected elements of the environment

The varied nature and specific properties of individual entities cause the number of these compounds to grow steadily. An increase in the production of nanoparticles leads to an increase in the volume of these substances in the environment, primarily—in sewage and sewage sludge, and consequently also in surface waters, sediments and soils. For example, the presence of fuel additives causes direct release of cerium oxide into the air during the combustion process. The compound then migrates further to waters and soils as a result of dry or wet deposition [54,55].

Apart from fuel additives, the products which use nanostructures of the highest risk to waters include paints, coatings, glues, cosmetics and hygiene products. The washing of nanomaterials from paints and coatings is fostered by a variety of meteorological factors, in particular—by precipitation. Scientists have found that over a year, from a panel covered with a paint containing silver nanoparticles, as much as 30% of nanosilver is washed out. At a later stage, its high reactivity results in the formation of bonds with sulphur as Ag_2S [56].

The most thermodynamically stable forms of most metals are their oxides. Among metal nano-oxides, high economic significance is attached to TiO_2, ZnO, AgO, Fe_2O_3, Fe_3O_4, CeO_2 and SiO_2 [57]. TiO_2 and ZnO, which display strong photocatalytic properties, are used in manufacturing of sun protection filters, paints and coatings. Manufacturing of only these metal oxides is estimated at 1,000 $\text{tons}\cdot\text{year}^{-1}$ [58].

Unfortunately, there has been no information about the number of nanocompounds, such as nanometals, in soils and bottom sediments. To convey the scale of the possible threat of soil and sediment contamination with nanometals, more information about nanocompound concentration in wastewater and waste (the major threat to the environment) is needed. For example, every year, ca. 320 tons of nanosilver in a variety of forms is used worldwide, a significant part of which is released into sewerage networks [59]. Study results have demonstrated that the quantity of silver nanoparticles released as a result of washing (and reaching water treatment facilities) may be up to 3,000 times higher than the current load [56]. It has been calculated that the content of nano-Ag in clothing was subject to change within the range from 0.003 to 1,400 $\mathrm{mg\,kg^{-1}}$ [60]. If it is assumed that in one year every inhabitant of an 180,000 agglomeration buys only one pair of socks with the highest nano-Ag content, the volume of this substance deposited into sewage will exceed 15 mg.

The results of the conducted study aimed at efficiency assessment of nanomaterials removal from sewage, with the application of standard treatment processes under laboratory conditions, have demonstrated that from 39 to 97% of nanosilver, 95% of cerium and copper oxide, as well as 23–95% of titanium dioxide are retained [61]. It must also be noted that technologies which are used in environmental purification and recultivation, including soil and water treatment and conditioning, may also pose one of the highest risks of nanomaterials migrating into soil and water (and then into sediments) due to release of nanometals built into the filter and membrane structure [62]. For example, iron nanoparticles like nZVI are used to inhibit sulphate-reducing bacteria in aquifer sediments [63]; iron nanoparticles like iron sulphide (FeS) nanoparticles are used to immobilise mercury in sediments [64,65]; haematite nanoparticles are used to adsorb As(III) and As(V), as well as subsequently controlling arsenic mobility and influencing any possible arsenic transformation in the environment [66].

Given that the volume of metal nanoparticles in sewage increases yearly, this is why in consequence of their increasingly common use in households and in industry as well as the lack of control over the extent of their removal, further migration of metal nanoparticles to surface waters and soil occurs. As a result, nanocompounds are introduced into the food chain [67].

Moreover, importantly, there is no information about what metal nanoparticle forms (e.g. nZVI, Fe–Al or other compounds) are present in soil or sediment samples. Such information is critical because it enables determining the bioreactivity of specific individual and associated hazards for the soil and aquatic organisms. Nitrification in the presence of various iron nanoparticle forms can be used as an example of the differential effect, which depends on the iron form and process duration; the final outcome is a variable reduction level of NH_4^+, and formation of NO_3^- [68,69].

3. Analysis of selected nanometals in solid environmental samples

Studies in occurrence and preservation of nanoparticles in soils are a relatively rare subject in the literature [70]. Existing studies concentrate primarily on nanosubstances' key properties which may play a part in determining their fate and behaviour in the soil, as well as on nanoparticle surface chemistry in relation to the capacity for interaction with organic and inorganic soil components. It must be noted that these studies are conducted under defined and controlled conditions related to the stability of nanoparticles (e.g. TiO_2, Ag, Fe_2O_3, CeO_2, CuO or ZnO) in soil suspensions and their transport behaviours in saturated soil columns [71–76].

The first stage of the analytical procedure is the preparation of the sample analysis—a complex and time-consuming process, which is often due to sample matrix complexity. The first step which initiates the entire analytical process is to collect and prepare the material. Sampling proves an important issue here, since during the procedure some significant errors are likely to occur and affect the final result of the determination. What matters especially in the case of metal nanocompounds is not only particle size, but also particle shape and bonds with other metals, nonmetals, and organic or inorganic groups.

The conducted studies have shown that in the case of solid environmental samples, as, for example, in bottom sediments or soils, the sampling and preparation stages are the same as in the case of standard analyses. It is very important not to dry the material at high temperatures due to the possible occurrence of mineralogical changes. Some authors recommend that the material should be first wet-sieved with the use of a sieve with the mesh size of 63 μm, and then—in ethanol through a sieve with the mesh size of 25 μm. Other researchers, in contrast, believe that the material first ought to be dried and only then—broken. It must be remembered that in both cases, the grinding and breaking must be done gently [77–79].

Wigginton et al. [80] have enumerated the following defining parameters which characterise nanomaterials found in natural media:

- Particle size distribution,
- area,
- direct rendering,
- phase and structure,
- chemical composition.

Unfortunately, no single analytical technique exists which would enable obtaining some information necessary to characterise nanoparticles in all these fields. That is why it is necessary to use a combination of a variety of analytical techniques. Moreover, nanomaterials from natural media may require size fractionation techniques in order to separate nanoparticles from bigger particles [79].

The ASTM Committee E-42 on Surface Analysis are to review and co-ordinate the development of standards for all surface analysis methods—with photon, electron, and ion emissions or reflection methods, such as X-ray spectroscopy and secondary ion mass spectrometry (SIMS) [79]. Analytical procedures in which analytical techniques, such as ICP-MS [81], HDC-ICP-MS [82,83] and FFF-ICP-MS [84] are used, are common. Hence conducted studies focus on testing advanced analytical tools [70,85–88], which include the following:

- Field flow fractionation in gravitational or centrifugal field (FFF),
- Size-exclusion chromatography (SEC), hydrodynamic chromatography (HDC),
- Laser-induced breakdown spectroscopy (LIBS/LIBD);
- Scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), scanning transmission electron microscopy (STEM);
- X-ray diffraction (XRD), X-ray fluorescence (XRF).

In addition, X-ray synchrotron microscopy may be used for functional identification of the carbon group which constitutes the base for nanoparticles [88]. X-ray spectroscopy provides some information on the crystal structure and may be used for characterising nanoparticle surface and coating, whereas nuclear magnetic resonance spectroscopy is used to determine the three-dimensional structure of nanoparticle samples [89]. New technologies, such as SIMS, may be applied to measurement of the size, structure and composition of individual particles [70]. However, only a few studies have aimed at development of techniques for determination of trace quantities of nanoparticles in environmental samples (such as the soil solution) or in food and fodder samples. This is because effective separation and collection of nanoparticles from natural systems poses some difficulty [87,89]. At various research centres, studies with the use of stable isotopes as markers in the analysis of a variety of environmental sample types (water ecosystems, soil matrixes, the atmosphere, animals, humans, etc.) for the presence of nanosubstances [90–92] are conducted in model systems.

The use of scanning microscopy enables viewing a virtual image on the monitor, rendered on the basis of signals sent by the sample. The system registers electron signals such as secondary electrons (SE), those emitted by sample atoms or reflected from sample material, as well as electrons which pass through the material (only in very thin samples). As a result of primary electrons' interactions with the sample, a variety of types of electrons are emitted which are used for the analysis of the chemical composition and for image rendering. These electrons include SE, back-scattered electrons (BSE) as well as Auger electrons, together with the emission of X-ray radiation. The signals generated during the electron-sample interaction reveal a lot of information about the studied sample, including morphology, the shape and size, chemical composition and the crystal structure, orientation of entities which are part of a given sample, as well as defects of the crystal structure.

As far as the study of nanomaterials is concerned, to understand their physical properties, in-depth knowledge of their structure (including the interphase surface, possible defects, down to the atomic level) is vital. This is why the apparatus often comes complete with a variety of detectors, including

- *Secondary electrons* (SE),
- *Back-scattered electrons* (BSE),
- *Energy dispersive spectroscopy* (EDS)—qualitative and semi-quantitative chemical analyses—does not detect very lightweight elements whose atomic number is less than 11, such as H, He, Li and Na,
- *Wavelength dispersive spectroscopy* (WDS)—comprehensive qualitative and quantitative analyses [93,94].

The scanning electron microscope continues to be one of the most important devices used for characterising micro- and nanomaterials as it provides some information on the size, morphology, the surface structure and the chemical composition of studied samples. The overall information, obtained during the analysis, allows one to draw some conclusions concerning the course of a variety of reactions and formation processes for a particular phase [93,94].

The asymmetrical flow field flow fractionation (AF4) is a new separation technique which enables fractionation of particles ranging in size from 1 to 10,000 nm. AF4 is currently becoming an increasingly common technique for fractionation and separation of macro- and nanoparticles. It belongs to the group of chromatographic techniques, based on a one-phase system. Diffusion is connected with Brownian motion, which in turn, causes counter-motion. Smaller particles, whose diffusion velocity is higher, tend to achieve equilibrium higher in the flow channel, where the longitudinal flow is faster. Due to this, the gradient of the inter-channel flow velocity enables the separation of particles varying in size. Smaller particles are transported along the channel much faster than the larger ones. The separation occurs in the flow channel, where the separating agent—instead of a stationary source—is the cross-flow perpendicular to the elution direction of the components (the channel flow). FFF may be combined with a variety of detectors in order to obtain a wide spectrum of quantitative and qualitative information on the sample. This is the case with, for instance, coupling to both multi-angle laser light scattering (MALLS) and high-resolution inductively coupled plasma mass spectroscopy (HR-ICPMS). MALLS enables obtaining the information on the size and shape of particles in the sample. HR-ICPMS, in turn, enables specification of the sample's chemical composition as a function of the particle size [95,96].

Relationships between trace metals and nanoparticles in riverbed sediment samples from the Clark Fork River in Montana (US) were investigated using analytical transmission electron microscopy (aTEM) and asymmetric flow field flow fractionation (aFlFFF) coupled to either MALLS, or multi-angle light scattering (MALS), and HR-ICPMS. In order to separate nanoparticles from the bottom sediment, water extraction was used. On the basis of the obtained results, it was found that metals bond with Fe and Ti nano-oxides [97]. The material was also examined using transmission electron microscopy and electron diffraction, coupled to energy dispersive X-ray spectroscopy, which makes it possible to identify which particular mineral phases and particle sizes host metals of interest. The obtained results have shown that trace metals in samples from riverbottom sediments of the Clark Fork river bond with iron and titanium nano-oxides, most frequently—with Geothite (crystallites ranging from several tens of nm to a few μm), ferrihydrite (crystallite sizes of this mineral approximate a few nm) and Brookite (TiO_2) [97]. In many cases, these were aggregates of nano-oxides and minerals which, as studies have demonstrated, behave differently than single mineral particles in the sediment [98].

Fraction separation enables obtaining the information on the volume of metal which occurs in the "nano" form in relation to the entire content thereof in the sample. The lack of possibility of conducting a speciation analysis limits the use of this analytical technique, particularly in view of the fact that in the case of nanocompound properties (toxicity, mobility, chemical activity, cancerogenicity and mutagenicity), it is not only the size of the nanoparticles that matters, but also their shape, structure and orientation.

The isolation of selected nanocompounds is often connected with the necessity of using appropriate eluates and introducing them into the solution. It must be remembered that handling the sample or any changes in the chemical environment during the analysis may significantly influence the properties of nanoparticles, particularly size distribution or chemical transformation. For example, the introduction of the dilution stage may accelerate the solution of particular types of silver nanoparticles and even cause agglomeration of the nanostructure depending on the coating or function groups which are present in the system [99]. Yet changes in the pH or the ionic strength usually have greater impact. They can affect not only the charge, but also a sterically stabilised nanocompound due to some chemical reactions such as changes of cross-linking or bonding between the polymer functionalisation centre and the nanoparticle core. In view of this, it is recommended that the behaviour of the anticipated or analysed nanoparticles in the environmental sample be verified with a rapid screening test (such as batch DLS) prior to the analysis for size-classified, chemical analysis like spICPMS (single particle inductively coupled plasma mass spectrometry) or A4F-ICPMS/MDA (the coupling of asymmetric flow field flow fractionation with inductively coupled plasma mass spectrometry). This kind of a screening test enables the assessment of possible results of dilution or other multimedia changes (e.g. the change in ionic strength due to addition of electrolyte surfactants, changes in the pH, and the like) during sample preparation or the analytical procedure, consequently preventing inaccurate results [99].

The charge of the nanoparticles may also affect separation efficiency and the recovery rate in an A4F-ICP-MS/MDA analysis. The charge of the nanoparticles and materials of which A4F fractionation membranes are made may cause some negligible changes of retention time [99,100]. These changes can be detected in particular in the case of varying sizes of nanoparticles smaller than 10 nm [99]. Some tests which would enable determination of the interaction between the metal nanocompound and the material of which the membranes are made are necessary. Only in this way will separation and the speciation analysis of nanometals become possible.

The A4F technique coupled with three detectors, UV, MALS and ICP-MS, was used to analyse bottom sediment samples from the Great Salt Lake, Utah (USA). Regenerated cellulose membranes (10 kDa) were used with Fl-70 carrier (0.1% and 300 ppm NaN_3). The conducted tests showed that a 10-nm nanoparticle of gold was better detected by the UV detector [101].

In some cases where (extensive) sample preparation is not feasible (e.g. direct coupling of analytical devices to ICP-MS, or time limitations in extensive test protocols), the uncertainties in the respective matrix should and can be easily addressed prior to an experiment [102]. One method of dealing with the solid environmental sample is to conduct separation and the quantitative analysis of the analytes in the solution. Nevertheless, some problems like time-dependent dissolution (dialysis), methodological and handling difficulties (CPE, centrifugation, TFF), or elevated costs (TFF) have to be considered. As a method suitable for different ENP suspensions, centrifugal ultrafiltration provides an easy to handle, moderately expensive tool for separation of the dissolved fraction from the particles [102].

The enormous diversity of metal nanocompounds emitted by humans into the environment makes it possible for structures varying in particle size, structure, chemical properties and biological activity to coexist. Studies conducted at various centres make it possible to obtain various forms of the same nanoparticles. All it takes is a change of the conditions of synthesis, for instance, such as temperature (Table 2) or pressure. Such a large diversity of forms in which one compound can occur causes the speciation analysis to require very accurate entity isolation and separation techniques.

It must also be noted that the co-existence of various nanocompounds, nanometals included, may lead to changes in size or surface type as well as grain size of individual structures. This is suggested by the results of XRD analyses of CeO_2 and CeO_2 with Fe_2O_3. The size of the CeO_2 crystallite was 17 nm, and upon the addition of Fe_2O_3, it dropped to 12 nm. The diffractogram also showed a peak which suggested the introduction of Fe on CeO_2 [104]. When the environmental material, such as soil or bottom sediment, contains various metal nanoparticles due to pollution or physical and biochemical processes which occur in the environment, it is necessary to separate individual entities for the subsequent quantitative analysis thereof.

It must also be said that the size of the nanoparticles, their build and set-up as well surface properties are subject to ongoing change in the environment as a result of interaction with other components and equilibriums which are shaped by a variety of bio- and geochemical factors. The literature on the subject contains some accounts of systems depicting the behaviour of nanocompounds in response to changes of a selected parameter (e.g. Cl^-, SO_4^{2-}, Ca^{2+}, pH, Gram-negative bacteria) present in the water medium and, to a lesser extent, in the soil medium. Study results suggest that humic acids present in the soils as well as the value of the ionic strength of soil solutions condition the mobility of metal nano-oxides, such as Fe_2O_4, TiO_2, CuO or ZnO [71]. Some authors, however, have observed that the processes of aggregation and modification of surface properties of iron nano-oxide are significantly affected by the pH value [105]. Studies on titanium dioxide [106] and gold nanoparticles [107] point to interactions between the particle and natural organic matter. This is why the process of sample preparation and the subsequent analysis must be conducted under very strictly specified conditions, the pH included, to guarantee the preservation of the analyte in an unchanged form.

During the analysis, some difficulties are posed by the systems in which metal nanoparticles occur next to each other, producing a signal in the area [108] similar to that of chromium and bismuth (Fig. 1). Under these circumstances, without specifying the conditions for the separation of individual entities, it

Table 2
Crystallographic data obtained from XRD for Fe_2O_3 synthesised under different conditions [103]

		Lattice parameters (Å)			
Phases present	Calcination temp. (°C)	*a*	*b*	*c*	L_{XRD} (nm)
γ-Fe_2O_3	100	8.3363	8.3363	8.3363	21.2
γ-Fe_2O_3	250	8.2680	8.2680	8.2680	24.5
γ-Fe_2O_3, α-Fe_2O_3	500	8.2331	8.2331	8.2331	25.8
α-Fe_2O_3	850	4.9876	4.9876	13.6114	42.3
γ-Fe_2O_3	100	8.5220	8.5220	8.5220	2.1
γ-Fe_2O_3	250	8.2915	8.2915	8.2915	8.6
γ-Fe_2O_3	500	8.2341	8.2341	8.2341	35.4
α-Fe_2O_3	850	4.9584	4.9584	13.5070	58.5

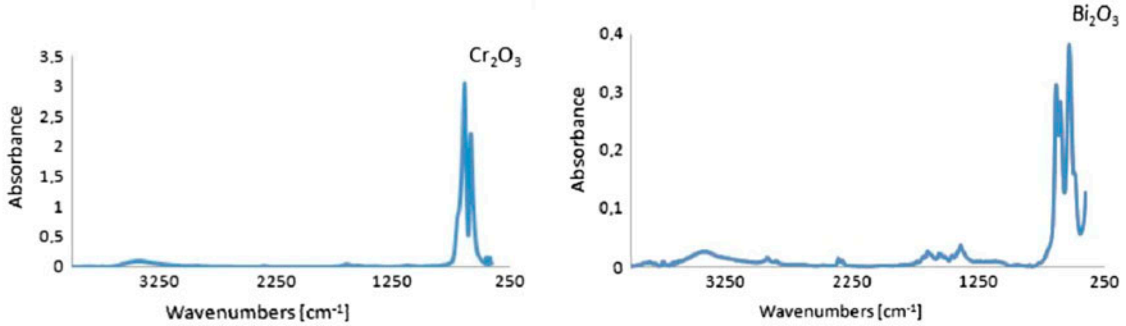

Fig. 1. An example of FT-IR nanoparticle spectrum of metal oxide powders (Cr_2O_3 and Bi_2O_3).

becomes hardly possible to conduct the analysis and accurately interpret the quality and changes occurring in the environment. [108].

Similar difficulties come from systems which contain metal nano-oxides of varying oxidation such as Co_2O_3 and CoO (Fig. 2).

The method proposed by Beneš et al. [109] which aims at determining the quantity of nZVI in the soil is worth noting. The method is based on the reaction of nZVI with sulphuric acid:

$$Fe^0 + H_2SO_4 \rightarrow FeSO_4 + H_2 \qquad (1)$$

In the case of iron coming into contact with H_2SO_4, three reactions can occur, however, each under different conditions. Reaction (1) occurs best at room temperature of ca. 21˚C and in the presence of 0% H_2SO_4 concentration. Volume measurement of the appearing H_2 enables volume determination of zerovalent iron on the basis of reaction (1) stoichiometry, as one mole of hydrogen is produced out of one mole of iron [109].

In the case of soils likely to be increasingly exposed to nanocompounds, there are no proper methods to study nanoparticle retention.

For the first time, the study [72] presented a method for determination of retention values (K_r) of Ag and CeO_2 nanoparticles that can be ranked among solid–liquid partitioning (K_d) values of bulk (micrometer-sized) forms, soluble salts and other possible soil contaminants that account for nanoparticle dissolution with the use of ultrafiltration (<1 kDa). Particle size distributions of spiking solutions were examined using DLS and different Ag concentrations; Ce(III) and Ce(IV) dissolved in artificial solution were filtered using commercially available membranes [72].

The conducted studies are based on very expensive techniques and methods, which require very advanced analytical apparatus, such as TEM, SEM or XRD. It must be noted that the studies are conducted in model systems, under defined and controlled conditions, which makes the transfer of the obtained information to real conditions in various environmental systems not always possible. Hence, the qualitative and quantitative analysis in real samples may prove problematic, particularly when speciation is taken into account, for example, necessary to specify bioavailability of a particular entity.

The qualitative and quantitative analysis which comprises as large as possible a number of nanometal features, and not only nanometal activity, gains in importance when organisms such as the *Bacillus sp.* bacteria demonstrate natural capacity for evasion of

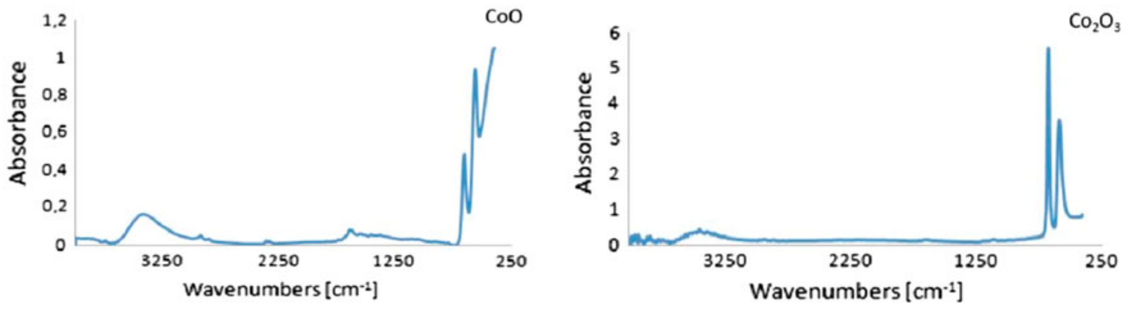

Fig. 2. An example of FT-IR nanoparticle spectrum of metal oxide powders (CoO and Co_2O_3).

cytotoxicological properties of nanosilver. Negative consequences of this fact may be particularly harmful given the common occurrence of the *Bacillus* bacteria spores in the air which may cause transfer of resistance genes to other micro-organisms [110]. The analysis of particular forms of nanocompounds, especially nanometals, is also important because of their impact on living organisms present in the soil or in the sediments, as exemplified by nano-TiO_2, which can be either toxic or not, depending on particle shape [111].

4. Conclusions

Increased production of nanoparticles leads to increased volume of these substances in the environment, in particular in sewage and sewage sludge, and —consequently—also in water, sediments and soils. The literature on the subject provides some information on metal nanocompound toxicity for a variety of organisms. This is why it is so important for the environment, human health and future sustainable development to understand the properties of nanoparticles as soon as possible. The varied build and size of metal nanoparticles, affecting varying characteristics and specific properties of individual entities, cause this group of compounds to increase in number. Determination of specific properties, such as the surface charge, solubility, aggregability, sorption surface size, as well as interactions with other organic or inorganic substances, carries fundamental significance for determination of their reactivity, and, as a result, for environmental risk assessment. Adequate assessment of these properties, however, requires some adequate analytical tools which enable effective separation and identification of individual nanoparticles as well as their aggregates [87].

Complex data concerning nanometal characteristics in solid environmental samples, such as bottom sediments, soils and biological material (plant and animal), are necessary to monitor their fates in the environment as well as assessment of their behaviours and possible migration routes [45,112–114]. The variability of nanometal properties, related to the measurement of these properties, must also be taken into consideration for risk assessment through application of adequate analytical, statistical and data management procedures so that the current and future quality and quantities of nanometals emitted into the environment might be fully described. The methods must be widely available, uncomplicated and inexpensive, as well as accurate and reliable to become commonly used by both research and control laboratories. Hence, it is necessary to develop some new methodological solutions and subsequent applications for analytical practice. It would allow researchers to obtain repeatable and reliable results which could provide the basis for adequate analytical interpretation.

At present, there exists no method that would permit quantity and form determination of nanometals present in the soil and sediments. Consequently, it is necessary to conduct further research in this area and, perhaps above all, in the field of pollutant elimination at source, that is from wastewater.

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