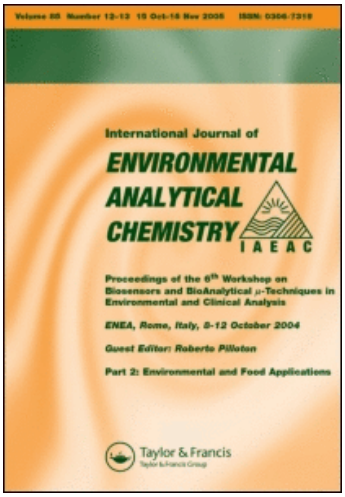

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Simultaneous determination of Cd, Cr, Cu, Ni, Pb and Zn in sewage sludge by slurry introduction ICP-OES method

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Simultaneous determination of Cd, Cr, Cu, Ni, Pb and Zn in sewage sludge by slurry introduction ICP-OES method

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In order to evaluate the slurry nebulisation method as an alternative method for analysis of sewage sludge, the metal content of sludge samples of different origins was determined. The concentrations of six elements: Cd, Cr, Cu, Ni, Pb, and Zn were determined by introducing the sludge as a slurry into an inductively coupled plasma optical emission spectrometer (ICP-OES). Calibration was performed by using aqueous standard solutions. For comparison, the sewage sludge was also digested by microwave digestion and introduced into the plasma as an aqueous solution. The accuracy of the method was checked by analysing a sewage sludge certified reference material (CRM 007-040 Sewage Sludge). The Student's *t*-test showed that values obtained using slurry nebulisation were close to the certified values at a 95% confidence level. The values of elements Cd 11.1 ± 0.8; Cr 37.7 ± 3.3; Cu 563.3 ± 38.4; Pb 119.2 ± 10.1; Zn $729 \pm 68.2\,\mathrm{mg\,kg^{-1}}$ obtained using this method were comparable with those obtained using the conventional method. The slurry method can, therefore, be successfully applied to the determination of content of each element in sewage sludge with RSD less than 3%, without the need to predissolve them. This could avoid the use of hazardous chemicals, incomplete dissolution and loss of volatile analytes.

Keywords: slurry introduction; ICP-OES; sewage sludge; metals

1. Introduction

Cadmium, chromium, cooper, lead, nickel, and zinc can be present as trace contaminants in all environmental compartments as a result of both natural and anthropogenic activities. The determination of those elements is of considerable interest because of their toxicity and ability to bioaccumulate in many organisms [1]. The knowledge of the toxicological implications of those elements in the environment has encouraged the development of very sensitive methods for their determination.

A significant increased level of heavy metals in the sludge is a strong argument against their use for fertilising purposes. Moreover, mineralization of sludge during its treatment does not decrease but increases the concentration of heavy metals. Facing increasing demands as to the properties of sludge admissible for agricultural use in Europe [2] including Poland [3], the amount of sludge used for that purpose has decreased.

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The admitted amounts of Cd, Cr, Cu, Ni, Pb, and Zn in sewage sludge, which can be used in agriculture are: 20–40; 100–1750; 1000–1750; 300–400; 750–1200 and 2500–4000 mg kg^{-1}, respectively [3]. In this context, an accurate and precise analysis of sludge and quick determination of Cd, Cr, Cu, Ni, Pb and Zn in sewage has become an important analytical task.

In the last decade, researches have analysed sewage sludge using different analytical techniques reporting the presence of heavy metals [4–14].

Decomposition of organic and inorganic matrices is a critical stage in trace metal analysis, since it largely determines the precision and accuracy of the obtained results. A wide variety of combinations of strong acids, oxidants, ultraviolet irradiation and elevated temperatures and pressure have been used and recommended. Main concerns are volatility and adsorption losses during elevated temperature digestion procedures, sample contamination, and the problem of using a large amount of reagents during pre-treatment, which gives rise to increased blank values and higher detection limits.

Slurry introduction is an attractive alternative to classical digestion methods because dissolution is so time consuming that sample preparation often requires more time than analysis. Slurry introduction is well-established for direct determination of trace metals in solids (ICP-OES). It has been widely applied to inorganic materials [12–14] and sediments [15,16]. The direct introduction of a slurry into ICP-OES reduces sample preparation time by combining matrix destruction, atomisation and excitation into a single step. It also reduces sample contamination, minimises analyte losses during preparation or due to incomplete release from the matrix and reduces the use of hazardous or corrosive reagents [17,18]. The transport efficiency of the slurry particle through the sample introduction system and behaviour of the particle in the plasma in terms of atomisation and excitation must be identical with those for a solution of equivalent concentration if aqueous calibration is to be used [19].

In this study, a procedure for rapid and simultaneous determination of six elements in sewage sludge is discussed using this approach. The special condition of using a suspension medium containing HNO_3 and HNO_3 + Triton X-100, solid particle size distribution measurements, influence of slurry concentration, calibration techniques and optimisation of operating variables were researched.

2. Experimental

2.1 *Instrumentation*

All measurements were carried out using a simultaneous spectrometer ICP-OES, model Vista-MPX, CCD Simultaneous (Varian Ltd, Australia). The sample introduction system consists of slurry quartz nebuliser, liberty axial model (Varian) and cyclonic spray chamber. The operating parameters and selected analytical lines are listed in Table 1. Slurries were homogenised using an ultrasonic processor model Sonopuls HD 2070 (Bandelin Electronic, Berlin, Germany) with a 3 mm titanium probe, allowing for the automatic agitation of the slurry. The radius distribution was determined by the use of dynamic light scattering (DLS) [19], where a laser beam is focused onto a region of the fluid and is scattered into a detector. The scattered light fluctuates in response to the molecular motion of the particles. From fluctuation in the scattered light, an autocorrelation function is determined, carrying information about diffusion time, size, shape and polydispersity of the sample (photon correlation spectroscopy (PCS)) [20].

Table 1. Instrumental operating conditions.

Spectrometer	Varian ICP-OES, model Vista-MPX, CCD Simultaneous
Power (W)	1200
Nebuliser	Slurry Quartz Nebuliser (Varian)
Outer argon gas flow rate ($l\,min^{-1}$)	15
Auxiliary argon gas flow rate ($l\,min^{-1}$)	1.5
Nebuliser argon gas flow rate ($l\,min^{-1}$)	0.9
Nebuliser pump (rps)	0.10
Analytical wavelength (nm)	Cd 214.43 Cr 267.71 Cu 327.39 Ni 231.6 Pb 220.35 Zn 213.86

The experimental set-up consisted of argon ion laser (Spectra Physics, USA, $\lambda = 488$) and a digital correlator ALV – 5000 E (ALV, Langen). The temperature of the sample was maintained within $\pm 0.01^{\circ}C$. The time-dependent photocount autocorrelation function was measured over a wide range of sample concentrations at the scattering angle of 90°. The function for which neither laser power dependence nor sample concentration dependence were observed were taken for the final analysis. In order to obtain the radius distribution function from the autocorrelation functions, the inverse Laplace transformation was applied (programme CONTIN) [21].

2.2 *Reagents and samples*

For wet digestion of samples, 65% v/v Suprapur HNO_3, and HCL supplied by Merck (Germany) were used. Calibrations curves were established using aqueous standards. The multielement standards (Cd, Cr, Cu, Ni, Pb and Zn) were prepared from $1000\,mg\,L^{-1}$ (Merck, Germany) aqueous standards (0.1; 0.5; 1.0; 3.0; $5.0\,mg\,L^{-1}$). Non-ionic surfactant Triton X-100 (Fluka, Switzerland) was used for dispersion of particles in slurry solution. All solutions were prepared in deionised water, distilled and passed through a Milli-Q water purification system from Millipore, USA. The blank and standards were prepared containing the same amount of dispersant.

2.3 *Material selected and slurry preparation*

Drying of the sewage sludge was done to ensure accurate and reproducible weighing. A conventional oven drying technique was used. The samples were put in the oven and dried at 100°C until constant weight was achieved. The dried samples were thoroughly ground by mechanically agates mortar (10 min.) then sieved by sieve of aperture of 30 μm. The resulting powder was kept in tightly closed plastic containers until analysis. Slurry was prepared by weighing homogenised sewage sludge samples and then transferring to acid – cleaned polypropylene autosampler cups containing following liquid media: 5.0% HNO_3 and 5.0% HNO_3 with Triton X-100. All operations were carried out in a clean bench. Three slurries were prepared for each sample and all measurements were carried

out in at least five replicates. Just before nebulisation, the slurry was agitated using an ultrasonic processor for 2 min at 50 W to ensure a stable and good dispersion.

In order to prepare stable and homogeneous slurry samples a liquid medium such as 5% HNO_3 and 5% $HNO_3 + 0.005\%$ Triton X-100 were used. Slurry was prepared by weighing 200 mg of homogenised samples of CRM 007-040 sewage sludge and quantitatively transferred into polypropylene autosampler cups after 50 mL liquid medium has been added to each cup. The slurries formed in this way were subjected to ultrasonic agitation for 2 min before measurement. After aspiration of each suspension, a 10% v/v HNO_3 wash was flushed through the nebuliser-torch system to remove any residual sample, minimising the chance of any possible memory effect. Calibration was performed by using aqueous reference solutions.

The following certified materials were analysed: CRM 007-040 (Sewage Sludge), BCR 146R (Sewage Sludge). The study was performed on three kinds of sewage sludge from a sewage purification plant in Poland: Koziegłowy (no. 1), Poznań (no. 2) and Gostyń (no. 3) and two certified reference materials.

2.4 *Microwave digestion*

For comparison, a microwave – assisted heating procedure was employed to digest sewage sludge samples. Approximately 0.5g of the sewage sludge preparation powder were accurately weighed into a PTFE vessel (100 mL total capacity). Ten millilitres deionised water, 5 mL of concentrated HNO_3 (60% w/v), 1 mL of hydrochloric acid and 4 mL of hydrofluoric acid were added, the vessel was capped and placed into the microwave oven model Mars 5 (CEM Corporation, USA) The heating programme was performed in one step: (1) the power of the process was 1200 W, (2) ramp time 25 min, (3) temperature 210 °C, (4) pressure 180 psi, (5) hold time 15 min. Blanks for control of the digestion process were prepared in a similar manner. The digested samples were quantitatively transferred into 10 mL volumetric flasks, and the final volume adjusted to the mark with deionised water.

3. Results and discussion

Although the results of the determination of Cd, Cr, Cu, Ni, Pb, and Zn content in the slurry were in accordance with those obtained by determination of CRM, the optimisation of several variables is necessary. For instance, the particle size, liquid media and stabilising agents, representative mass and mass/volume ratio, partitioning and measurement procedure (calibration, precision and accuracy) may influence the results.

3.1 *Number and size of particles*

The distribution of the particles and their diameters determined for sewage sludge from certified material (Sewage Sludge CRM 007-040) and three sewage sludge real samples from the Wielkopolska region are shown in Figure 1. For the certified reference material the particle diameter varied from 50 to 700 nm (mean value was 290), whereas for the real samples of sewage sludge it was similar and varied from 50 to 900 nm (mean value for sewage sludge no. 1 was 352 nm, for no. 2 was 655 nm and for no. 3 was 467 nm). The number and size distribution for CRM and three real samples from the Wielkopolska region were comparable. In the slurry introduction method, application of particles

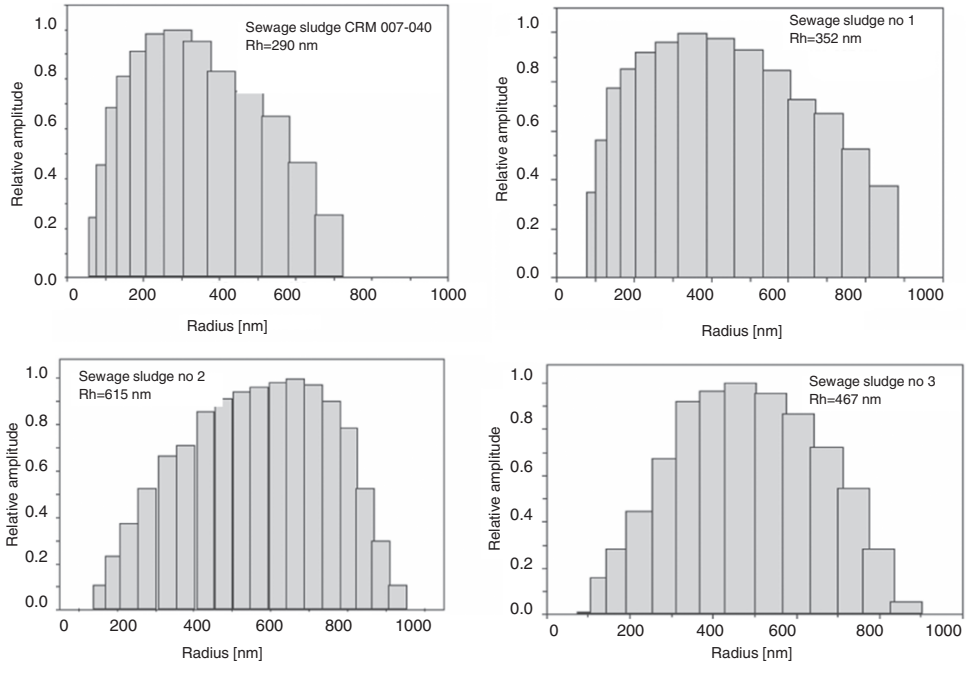

Figure 1. Particle size distribution of the radius (nm) in the slurry for CRM sewage sludge 007-040 and sample.

smaller than 2 μm is recommended. In case of particles size greater than 2 μm the slurry sample can not be comparable to solution [22].

3.2 *Slurry stability*

Signal intensity remained constant for 5% HNO_3 and 5% $HNO_3 + 0.005\%$ Triton X-100 (Figure 2) for all elements with the exception of Cr, which showed slight decline. This observation highlights the significance of HNO_3 in preparing stable slurries of sewage samples. Signal stability for 30 min is satisfactory, as most ICP-OES analysis require signal acquisition times of less than 2 min. In order to check whether the long duration of stability of suspension is not the result of an effect of memory, a second sample was prepared and checked by the intensity of signal after a longer time of washing by using a washing agent of 10% HNO_3. The results of both analyses were similar. The problems with sedimentation of suspension often appear during analysis of solid samples by slurry nebulisation method. Forming the large agglomerates of particles and their quick falling are caused by the increase of sedimentation in suspension [12]. The use of stabilising medium limits the sedimentation of solid particles in the solution. The stabilising medium has an influence on easy dispersion of solid particles in the solution. One of the most often used stabilising mediums for preparation of homogeneous suspensions of varied samples is Triton X-100 [14,23,24,25]. Application of stabilising medium has a favourable influence on transportation of suspension to plasma, this was proved in the paper written by Halicz *et al*. [26] and Brenner *et al*. [27]. The concentration of stabilising medium depends on kind and quantity of the studied sample. In case of geological materials such as: soil or sludge,

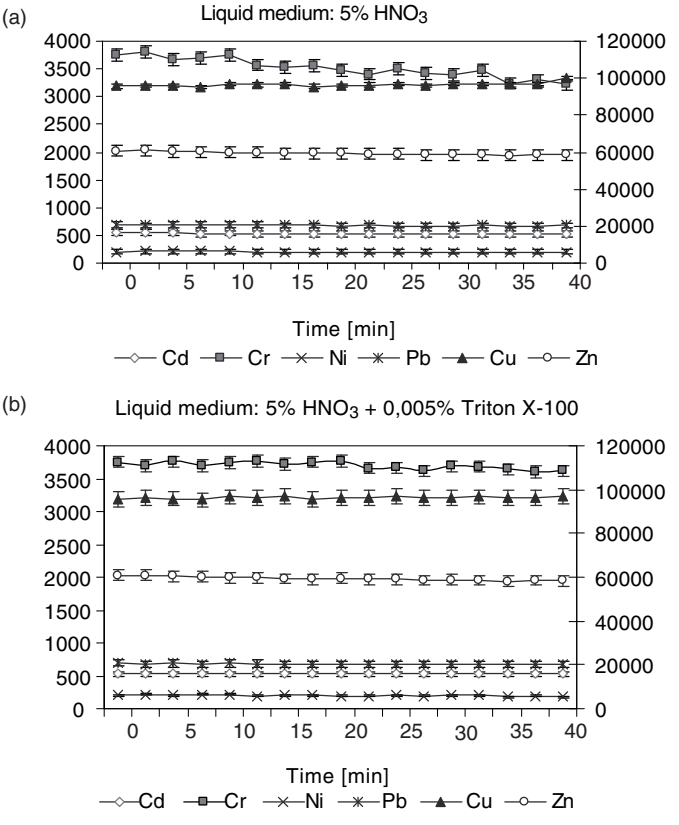

Figure 2. (a, b) Variation of emission intensity with slurry aspiration time under static conditions in the determination of Cd, Cu, Cr, Ni, Pb, and Zn in slurries prepared in two liquid mediums (±SD; $p > 95\%$, $n = 5$).

solutions with concentrations lower than 0.5% are applied [24,25,28]. Too high concentration of stabilising medium may cause sample foaming, that unfavourably influences accuracy and precision of measurement [14,29].

3.3 *Slurry concentration*

Another critical factor for slurry preparation is slurry concentration. Introduction of representative part of sample to plasma is connected with suitable relation of sample mass to liquid medium volume. Diluted slurries with varying concentrations were prepared and emissions of the signals for the CRM samples were acquired. Figure 3 shows variation of emission intensity of Cd, Cr, Cu, Ni, Pb, and Zn according to concentration of slurries during slurry introduction. Concentrations of slurry of sewage sludge from 0.05 to 0.4% w/v were examined. The most optimal slurry concentration was 0.2% w/v. Multielement analysis of one sample required finding a common value of slurry concentration for all determined elements. Usage 0.2% w/v slurry concentration enabled the determination of content of each element with RSD less than 3%. With the higher concentration, a trend towards emulsion formation was observed. The lower limit of this concentration depends on the content of the analyte in the sample and is also determined by the necessity to preserve

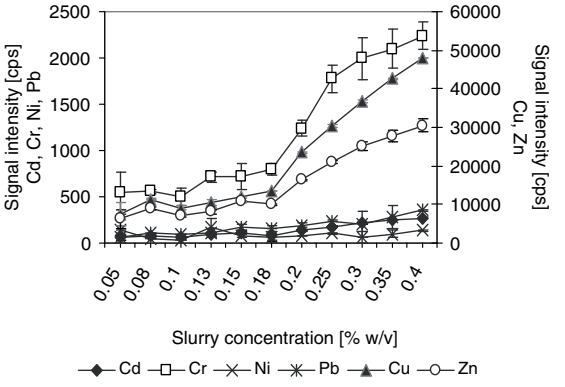

Figure 3. Variation of emission intensity of Cd, Cu, Cr, Ni, Pb, and Zn with concentration of slurries determined during slurry nebulization CRM ICP-OES (±SD; $p > 95\%$; $n = 5$).

Table 2. Percent of suspension dissolved in the liquid medium.

	Concentrated liquid medium/concentrated slurry ×100%					
Liquid medium	Cd	Cr	Cu	Ni	Zn	Pb
5% nitric acid	57.1	36.8	78.2	34.7	82.5	85.3
5% nitric acid + Triton X-100	56.3	34.2	74.7	31.5	79.7	83.3

a representative mass of the sample. Consequently, Miller-Ihli [11,30] has introduced the notion about a 'representative mass of a sample'. This means that the sample fraction to be used for slurry preparation must be representative and the injected slurry aliquot must also be representative.

Liquid medium also has an influence on extraction of analyte to liquid phase [31,32]. Higher extraction degree of analytes to liquid phase increases the precision of measurement to a level which is comparable with analysis of liquid samples [18]. The growth of extraction degree of analyte to solution is achieved through use of inorganic acids and application of a homogenised system of liquid medium for preparing suspensions [18,33,34]. In order to verify the extraction degree of analytes (Cd, Cu, Cr, Ni, Pb the and Zn) from solid phase to liquid phase in dependence of applied liquid medium, analysis of filtrates after 2 minutes of sample homogenisation was conducted. Results of analysis are presented in Table 2. For CRM sewage sludge 007-040 the extraction of Cr and Ni conducted with use of medium (HNO_3 and HNO_3 + Triton X-100) does not exceed 36.8% while that, for Pb, Cu and Zn it is higher and equal to 85.3, 78.2 and 82.5%, respectively. The level of analytes extraction to the liquid phase does not depend on the medium, which was used but instead depends on the analysed element and matrix of the sample. Moreover, similar results for Cd, Cr, Ni, and Pb studied were reported by other authors [18,20].

3.4 *Measurement procedure*

To evaluate the use of aqueous calibration standards in slurry analysis, calibration curves were obtained for Cd, Cr, Cu, Ni, Pb and Zn to be determined using standard solutions

and standard suspensions made of CRM sewage sludge 007-040. Suspensions of samples (CRM 007-040 sewage sludge) with increased relation of mass sample to volume of medium were prepared, which is connected with growing concentration of determined elements. Prepared samples were used for calculating the calibration curve. Calibration with use of water standards was applied as a comparative method. Concentrations of particular standard were in response to concentration of analysed elements in certified reference material. Comparison of calibration curves for both methods of calibration was conducted for all determined elements. Results are presented in Figure 4. The T^2 Hotelling's test (with a confidence level of 95%) was applied to compare the calibration. The slope of the linear regression coefficient was calculated and shown in the case of each element in Figure 4. Based on the slope values, it was found that the results of Cd, Cr, Cu, Ni, Pb and Zn analysis are in agreement with the two analytical methods. The calibration curve constructed using water standard solutions may be successfully applied if some criteria such as appropriate size of particles are retained. Proper results obtained from analysis of given elements using the calibration curve prepared on water standard solutions were observed in the case of other slurry samples such as: cement, gypsum, sediment, nutrients and powder milk for children [31–34].

The results obtained using the slurry nebulisation ICP-OES method were compared to the results obtained from the wet digestion method and the results from reference material CRM 007-040 sewage sludge analysis. The significance of the numerical deviations seen in Tables 3 and 4 was estimated by the statistical Student's test method.

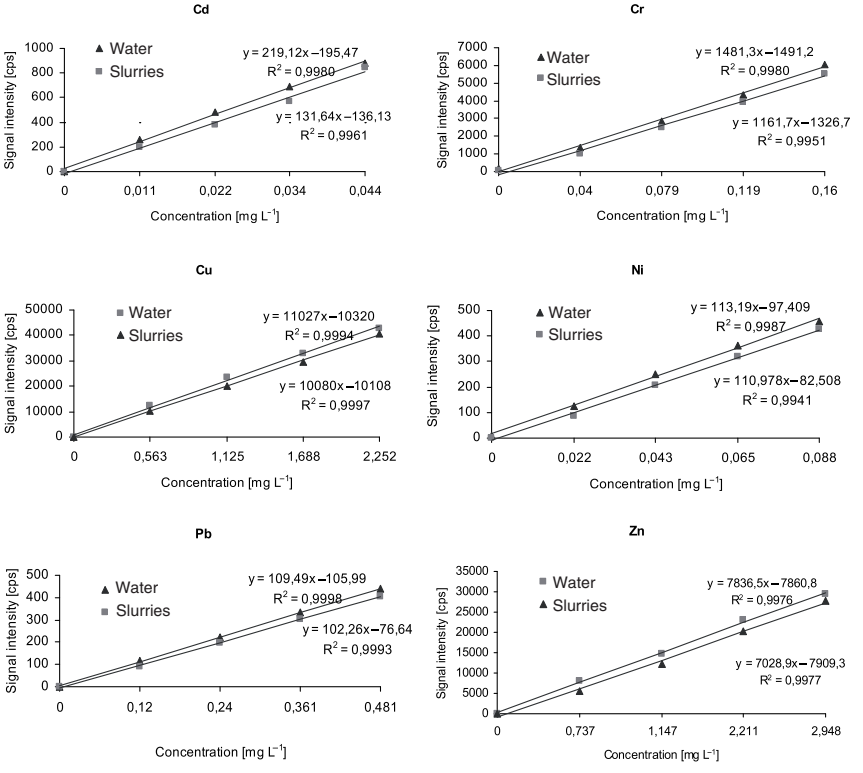

Figure 4. Calibration curves for Cd, Cu, Cr, Ni, Pb, and Zn.

This indicates that there were no significant differences between the results obtained by the slurry method and the wet digestion method. Similar statements are valid for the comparison of the results obtained by the proposed method for CRMs and their certified concentrations.

Precision, expressed by the standard deviation SD, depends on the content of a given element in the certified material reference studied and on the method of its determination. The precision (RSD) of the slurry nebulisation method ICP-OES is $<10\%$, whereas that conventional method is always $>10\%$.

Table 3. Analytical results (mean $\pm$ 1s) for the analysis of sewage sludge CRM 007-040 using aqueous standards for calibration ($n=5$; $P=95\%$).

Element	Acid digestion value obtained, $\mu g\,g^{-1}$	Slurry nebulisation value obtained, $\mu g\,g^{-1}$	Certified value, $\mu g\,g^{-1}$
Cd	10.9 ± 1.6	11.1 ± 0.8	11.4 ± 1.4
Cr	35.4 ± 6.2	37.7 ± 3.3	39.7 ± 7.1
Cu	561.2 ± 51.1	563.3 ± 38.4	562.6 ± 46.4
Ni	21.2 ± 4.4	21.4 ± 1.8	21.6 ± 3.6
Zn	734.2 ± 78.6	729.5 ± 68.2	736.9 ± 72.4
Pb	119.7 ± 12.9	119.2 ± 10.1	120.2 ± 11.6

Table 4. Results obtained (mean $\pm$ 1s), for analysis of slurry sampling and wet digestion of sludge from sewage purification plants in the Wielkopolska region, Poland ($n=5$; $P=95\%$).

		Result obtain, $\mu g\,g^{-1}$	
Element	Samples	Slurry sampling	After wet digestion
	Sludge Koziegłowy no. 1		
Cd		6.1 ± 0.5	5.8 ± 0.7
Cr		132.9 ± 10.2	134.9 ± 13.5
Cu		855.5 ± 66.2	855.3 ± 99.1
Ni		125.1 ± 8.1	124.1 ± 12.6
Pb		65.5 ± 5.4	62.3 ± 6.3
Zn		1092.5 ± 91.4	1089.4 ± 109.2
	Sludge Poznań no. 2		
Cd		6.7 ± 5.1	6.6 ± 7.2
Cr		74.6 ± 6.8	71.3 ± 7.0
Cu		361.6 ± 38.4	364.5 ± 38.2
Ni		50.1 ± 4.3	50.6 ± 5.7
Pb		31.6 ± 2.3	29.9 ± 3.4
Zn		807.4 ± 61.4	802.2 ± 78.1
	Sludge Gostyé no. 3		
Cd		4.4 ± 0.3	4.4 ± 0.4
Cr		316.1 ± 26.4	315.8 ± 34.2
Cu		159.2 ± 12.9	156.9 ± 17.4
Ni		21.3 ± 1.7	22.1 ± 2.5
Pb		33.2 ± 2.8	31.9 ± 3.5
Zn		850.1 ± 75.1	855.3 ± 89.6

Table 5. Parameters characterising the method.

Parameters	Cd	Cr	Cu	Ni	Pb	Zn
LOD, $\mu g\,g^{-1}$	0.2	0.5	0.9	0.7	1.5	0.2
Precision, %RSD	2.3	2.9	0.9	2.1	1.2	2.5
Recovery, %	102	97	99	98	99	99

The analytical data from sample analysis CRM 007-040 are in conformity with the certified values (Table 3). The concentrations of Cd, Cr, Cu, Ni, Pb, Zn, determined by the conventional method are lower, which can be explained by incomplete mineralisation of sewage sludge or the loss of the analyte during sample preparation (Table 4).

The detection limit (LOD) was estimated using the 3σ for 10 successive determinations of the blank. The precision was calculated using the relative standard deviation for 10 successive determinations. The values of these parameters can be found in Table 5. This is comparable with the precision of 2–17% RSD according to the determined elements (e.g. Cr, Cu, Ni, Zn), which were obtained in geological samples [26]. Halmos *et al*. obtained the precision of 1–5% while elements determination in fly ash materials by ICP-OES with slurry introduction [36]. Carrion *et al*. obtained better precision for slurry sampling (~1%) than for wet ashing (~2%) [39]. Thus, the precision of the slurry method is similar to the conventional acid digestion.

4. Conclusions

Slurry sample nebulisation is an alternative method to solution nebulisation and has received particular attention in recent years. The proposed method, rapid ICP-OES determination combined with slurry introduction, is simpler and faster than those previously reported for Cd, Cr, Cu, Ni, Pb and Zn in sewage sludge, and thus is attractive for routine simultaneous determination elements of low trace element levels in sludge as an index of environmental exposure.

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