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Investigation of analytical procedures developed in the CEN-project HORIZONTAL towards their applicability on conventional and sewage sludge derived secondary fertilizers

Summary

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Investigation of analytical procedures developed in the CEN-project HORIZONTAL towards their applicability on conventional and sewage sludge derived secondary fertilizers

Summary

by

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1 Summary

1.1 Background

In Germany the application of relevant amounts of sewage sludge in agriculture and land scaping started when landfilling was prohibited due to regulations that were set in force 1993 (TA Siedlungsabfall 1993). However, this form of utilization continuously decreased till the late 1990s due to the awareness of organic and inorganic pollutants present in sewage sludge. As sewage sludge is the sink for pollutants in the waste water treatment plant, this concern is generally justifyable. Pollutants in sewage sludge can be organic, such as antibiotics and other pharmaceuticals as well as personal care products or inorganic such as heavy metals. Some of the pollutants are summarized as Emerging Pollutants of Concern (EMPOC). Organic pollutants can be easily and safely destroyed by incineration. The resulting sewage sludge ashes are free of organic pollutants and still contain nutrients such as phosphorus, calcium, potassium and magnesium. However, the heavy metals present in sewage sludge are also still present in the related ashes. Sewage sludge ashes are in most of the cases deposited under ground or are applied for landfill, mine filling, and road construction. The nutrients are lost for fertilization in agriculture in this case. Sewage sludge and sewage sludge ashes are relevant secondary raw materials for nutrient recovery. Further relevant nutrient carrying secondary raw materials are different waste streams from food production and by-products from the treatment of different nutrient bearing wastes and waste waters. There are some good reasons for the position, that the above mentioned secondary raw materials should be treated aiming at nutrients recovery and re-introduction into the economic cycle. In this context it is of urgent necessity that the newly accruing recycling fertilizers are thoroughly investigated to assess its fertilizing effect as well as its hazard potential.

The European Union is aiming at transnational harmonized regulations to guarantee an effective execution as far as possible. In front of this background the EU commissioned the European Committee for Standardization (CEN) with the mandate M330 aiming at the development of new analysis methods for inorganic and organic parameters that are applicable to a broad range of different matrices such as sewage sludge, compost and soil. Those analytical methods, developed by CEN, were then validated for different materials within the framework of the UFOPLAN-project HORIZONTAL (3711 26 325) and were established in form of horizontal standards in order to include them in European and national regulations such as ordinances for the regulation of sewage sludge or biowastes. The approach of horizontal standardization aims at simplification and optimization of the practicability of execution of divers regulations that rely on a manageble number of horizontal standards. Furthermore, a transnational harmonization is envisaged as well as a comparability of results. Additionally, it is expected that laboratories must not handle a divers array of different methods. Recently, the European Commission has commissioned an investigation on the effects of a harmonized European fertilizer ordinance. Technical and economic effects were considered in this study as well as environmental and societal effects. The ammendment of the EU fertilizer ordinance (EG) 2003/2003 will be based on the results of that study. Besides the multitude of existing and new fertilizer types, such as recycling fertilizers, also organic fertilizers and matrices such as sewage sludge, biowastes from digestion plants and manures should be regulated by this ordinance. This means that parameters and limit values currently regulated in different ordinances will be regulated in one ordinance in the future (e.g. fertilizers and sewage sludge). Furthermore, new materials must be included in the new ordinance. It can be expected that the number of very different recycling fertilizers will increase in the near future as agricultural utilization of sewage sludge will decrease due to a new policy and new regulations aiming at protection of arable land and resources conservation (e.g. ProgRess). The amended sewage sludge ordinance (AbfKlärV) was approved on 18.01.2017 and regulates that after a transition period all large waste water treatment plants will have to recover phosphorus from sewage sludge or sewage sludge ash. Thus, phosphorus recycling fertilizers from sewage sludge or sewage sludge ash will be relevant secondary fertilizers to be considered in the near future.

Regarding the background described above it is required to assess the applicability of existing analytical standards for sewage sludge, sewage sludge ashes and secondary raw materials derived from those sources. The aim of the research project was to investigate if existing analytical methods for fertilizers can be applied on new recycling fertilizers, independently from their respective matrices. The methods identifyed applicable can be used for new horizontal regulations in progress. Furthermore, the results of this study should be used to improve existing standard methods towards its applicability on the new recycling fertilizers. Investigations on the robustness of the methods should include the sample preparation.

1.2 Goals of this Project

The aim of the research project was to investigate if existing analytical methods for fertilizers can be applied on new recycling fertilizers, independent of their respective matrices. The general applicability of the established analytical methods for fertilizers including sample preparation was thus applied to a broad spectrum of different recycling fertilizers. The major aim was to find out if the analytical methods can be applied to the new recycling fertilizers and if there are matrix related effects influencing the results significantly. The robustness of the analytical methods should be investigated and suggestions for optimization of the methods should be derived from the results. The results of this study should be used for further investigations on method validation.

1.3 Methodologies and Quality control

Sample acquisition was based on existing networks and by an intense inquiry. A total number of 67 samples of very different origins were collected and used for the investigation. The array of different samples consisted amongst others of sewage sludges, recyclates from municipal waste water and sewage sludge (e.g. struvites, products from the P-Roc process), recyclates from industrial wastewaters (struvite), sewage sludge ash and related recyclates (e.g. AshDec), vinasse, animal wastes and by products (e.g. meat and bone meal and chicken manure), by products from the steel industries (slags), biochars, phosphate rocks and conventional fertilizers (e.g. TSP, NPK-, potash- and ammonium sulphate fertilizers). A list of all samples can be found in Table 4 (section 4.1, page 28).

The samples were prepared by air drying and representative subsampling before starting the analytical investigations. Depending on the target of the analytical procedure the samples were milled in a tungsten carbide grinding set.

Water content and loss of ignition were determined after DIN 18128, 2002-12 using the air dryed samples. In case of thermolabile substances such as struvite, samples were also dryed at a temperature of 40°C.

The total organic carbon content (TOC) was determined in the lab of the German Environmental Protection Agency after DIN EN 13137 using a „vario TOC cube“ of the company Elementar. The air dryed samples were treated with chloric acid (10%) to remove the inorganic carbon. The treated samples were incinerated at 950°C and the carbon content measured in the offgas.

After application of different microwave assisted digestion methods the element mass fractions were determined by ICP-OES or ICP-MS. Additional to the commonly used aqua regia digestion (Aqr) an inverse aqua regia digestion (Inv), a digestion with $HClO_4/HNO_3/HF$ (Per), a H_2O_2/HNO_3-digestion (ox), a $H_2O_2/HNO_3/H_2SO_4$-digestion (s) a digestion with NaOH (a) were comparatively investigated. The aim was the comparison of the digestion performances depending on matrix and element. An overview of the suitable digestion methods should be given as well as an overview about underestimations if standard methods are used for digestion. The elements Al, Ag, As, Ca, Cd, Co, Cr, Cu, Fe, Ga, Ge, Hf, Hg, K, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, S, Sb, Se, Si, Sn, Sr, Ta, Th, Ti, Tl, U, V, W, Zn and Zr as well as the elements of the rare earths were analysed.

Due tot he high number of different matrices and the fact that for most of them no reference materials are available, quality control by reference material was very limited in this study. In a former UFOPLAN-project (37 11 33 321, "monitoring of sewage sludge ashes", UBA Texte 49/2014) a coal fly ash (CTA-FFA-1; Instiute of Nuclear Chemistry and Technology, Laboratory of Nuclear Analytical Methods, Warsaw, Poland) was used for quality control and optimization of the analytical methods. Furthermore, two types of sewage sludge ashes (high and low ferric content) were characterized very thoroughly by reconstitution analysis and were used as an "internal reference material" for the investigation.

Among the group of plant nutrients, phosphorus was in the focus of the investigation. Investigations on the solubility in water (P_{wlk}) and neutral ammonium citrate solution (P_{NAC}) were carried out. The influence of parameters such as the extraction time, the extraction temperature, the type of filtration and the samples preparation by milling were investigated in order to identify matrix related sensitivities.

Hexavalent chromium (Cr(VI)) was selected as an important pollutant for an extended investigation program. According to the fertilizer ordinance Cr(VI) is a regulated pollutant (limit value 2 mg/kg) that is analyzed after EN 15192 (DIN EN 15192, 2006). In this study robustness tests were carried out in order to identify matrix related problems of the analytical procedure. In this context the sensitivities of the parameters extraction temperature und -time were investigated. Spiking experiments with Cr(III) and Cr(VI)-species were carried out for quality control. Batches of separate experiments were spiked with soluble Cr(III), soluble Cr(VI) or with a hardly soluble Cr(VI)-compound. Those spiking experiments were conducted in order to find out if matrices have the potential to either oxidize Cr(III)-species or reduce Cr(VI)-species and thus lead to false results.

Some selected samples were analyzed for the 16 relevant PAH according to EPA (EPA-PAH) after DIN ISO 13877: 2000-01. Samples of different types of matrices were chosen for this investigation. Biochars were of special interest for this investigation as they bear the potential of being contaminated by PAH due to the conditions during their production. All measurements were carried out in duplicates.

1.4 Results

1.4.1 Samples preparation and determination of the phosphorus solubilities

Thermolabile substances such as struvite (magnesium ammonium phosphate) have to be dryed at temperatures lower than the standard drying temperature of 105°C. If struvite is dryed at a temperature of 105°C (DIN 18128, 2002-12) it decomposes. In this study mass losses of 30-50% were determined by using the standard method. Those mass losses were not due to evaporation of water but due to thermal decay of struvite. Besides wrong interpretation of the determined value as water content, the sample is not suitable to be used for subsequent investigations. Of course, thermal decay changes the mineralogical chemical composition of the sample and would lead to false results if used for further investigations. Struvite releases ammoniac and water due to thermal decay and thus forms different magnesium phosphates with different characteristics. The phosphorus solubility in ammonium citrate solution of struvite dryed at different temperatures (40°C/105°C) were however still at the same level. It can be assumed the magnesium phosphates formed after thermal decay had also a good solubility in ammonium citrate solution comparable to struvite. Probably, soluble $Mg(H_2PO_4)_2$ and/or $MgHPO_4$ were formed under the moderate conditions of drying at 105°C. A stronger effect of thermal decay was observed when struvite was milled. Milling locally causes much higher temperatures than 100°C and most probably lead to the formation of hardly citrate soluble forms such as $Mg_3(PO_4)_2$. For milled struvites as well as for milled TSP the determined P_{NAC}-solubilites were significantly lower compared to samples that were not milled.

The filtration method also had an effect on the results of the P_{NAC}-solubility. Simple folded filters have to be used after method DIN EN 15957, 2011-12. However, some laboratories use membranefiltration in order to protect their analytical equipment such as an ICP-OES. For all investigated samples the P_{NAC} values determined after filtration by folden filters were significantly higher compared to those determined after pressure filtration through a membrane. The results can be explained by the rejection of fine P-bearing particles by the membrane. Thus the filtration method has to be considered when comparing the results. Another effect observed was the lower standard deviation of the results achieved by application of the membrane filtration instead utilization of folden filters. The latter have a separation cut that is not sharp and not defined. Thus, the rejection of fine particles can vary leading to a higher standard deviation. In order to reduce the standard deviation of the method for the determination of the P_{NAC}-solubility we recommend the utilization of membrane filters instead of folden filters.

Depending on the matrix also the parameters extraction time and extraction temperature may have an influence on the result of the P_{NAC}-solubility. For some sample matrices such as the products from the P-Roc process no significant differences of the P_{NAC}-solubility (average 80%) were observed even over broad ranges of extraction time (30-90 min) and extraction temperature (60-70°C). For hardly soluble sewage sludge ashes and phosphate rock a trend to higher extraction at higher extraction time and higher extraction temperature was observed. In case of struvite and also for TSP the extraction was significantly higher at an extraction temperature of 70°C compared to the just slightly lower standard extraction temperature of 65°C. Thus, these matrices are sensitive to the variation of the extraction even in small temperature ranges. In case of the struvites even the lower extraction temperature of 60°C lead to a higher P_{NAC}-solubility which can be hardly explained. The finding of the lowest value for the determined P_{NAC}-solubility at an extraction temperature of 65°C was also confirmed for sewage sludge from the digester that potentially also contains struvite. The findings of this study show that 65°C might be an extraction temperature which is unfavourable for those matrices containing struvite. This phenomenon should be further investigated to avoid false interpretation of the results.

1.4.2 Element mass fractions – Performance of digestion methods

The performance of the 6 digestion methods was comparatively investigated. The digestion solutions were analyzed by ICP-OES and/or ICP-MS. All results are listed in tables 56-120 in the appendix. Furthermore, a qualitative overview over the most effective digestion methods for each element-matrix-combination can be found there.

In this study the nutrients phosphorus, calcium, potassium, magnesium, sodium and sulfur were investigated more comprehensively. The maximum element mass fractions determined for the different investigated materials can be found together with the respective analytical procedure in Table 1. Due to the fact that also single nutrient fertilizers that contained only one of the nutrients were part of the study, the minimum contents were all far below 1%.

Table 1: Maximum nutrient mass fractions of the set of analyzed materials and the respective analytical procedure

Nutrient	Maximum mass fraction [%]	Digestion method	PN	sample	Analytical procedure
P	24,21	Inv	26	TSP	ICP-OES
Ca	37,78	Inv	40	P-Roc	ICP-OES
K	29,52	Inv	27	MG-K	ICP-OES
Mg	13,6	Per	6	MAP	ICP-OES
Na	13,00	Per	60	KSA+	ICP-OES
S	5,94	Inv	27	Mg-K	ICP-OES

The table shows that the maximum values were either determined after digestion with the inverse aqua regia digestion method (Inv) or the digestion method with perchloric, nitric and hydrofluoric acid (Per). However, in general the results after digestion with aqua regia were also at the same level. A simplifyed summary of the results is that for the determination of the nutrients the three digestion methods Per, Inv and Aqr are generally applicable and lead to comparable results whereas the other three investigated digestion methods "ox", "s" and "a" in some cases showed underestimations. A qualitative summary of the most efficient digestion methods per element and matrix can be found in Table 3. This summarizing table was already optimized in terms of minimization of the number of digestion methods that are required. It can be seen that the "Per" digestion is in many cases the best choice as it was efficient independently from the very different matrices investigated. In many cases also the digestions "Aqr" and "Inv" were alternatives for the "Per" digestion and don't lead to remarkable underestimations.

In this study the trace elements arsenic, cadmium, mercury, nickel, lead, thallium und uranium were chosen for extended investigations towards the performaces of the 6 digestion methods. The table below (Table 2) lists the minimum and maximum mass fractions out of the investigated samples together with the respective analytical methods. In contrast to the analysis of the main nutrients it can be seen that also the oxidative digestion methods with and without sulfuric acid ("s" and "ox") showed in two cases the highest performances out of the digestion methods. A summary of the most suitable digestion methods for the different element-matrix combinations is again suggested in Table 3.

Table 2: Summary of the trace element contents (min/max) of the samples

		Maximum Values				
Trace elements	Minimum [mg/kg]	Maximum [mg/kg]	digestion	PN	sample	Analysis method
As	0,60	38,90	Aqua regia	42	P-Roc	ICP-MS
Cd	0,12	17,70	H_2O_2/HNO_3	40	P-Roc	ICP-MS
Hg	0,01	2,95	Aqua regia	13	KSA	ICP-MS
Ni	5,93	67,93	Per	13	KSA	ICP-MS
Pb	3,66	91,71	Per	16	KSA	ICP-OES
Tl	0,22	0,42	Per	13	KSA	ICP-MS
U	0,16	223,95	$H_2O_2/HNO_3/H_2SO_4$	40	P-Roc	ICP-MS
Zn	74,29	2359,64	Inv	13	KSA	ICP-OES

Table 3: Suggested digestion method depending on the investigated element-matrix combinations oriented on a minimum number of required digestion methods

	7; entw. FS	14; DS	46; HTK	47; FKM	6; MAP 1	18; MAP 2	13; KSA 1	16; KSA 2	60; KSA+	8; sek.P-Roc	9; sek.P-Roc	11; KK42	40; P-Roc	42; P-Roc	26; TSP	27; Mg-K	Per	Aqr	Inv	ox	s	a	-
P	Per	Per	Inv	Inv	Per	Per	Per	Per	Per	Per	Per	s	Per	Per	Per	-	12	0	2	0	1	0	1
Ca	Per	Per	Inv	Inv	Per	Per	Per	Per	Per	s	Per	Per	Per	Per	Per	Per	13	0	2	0	1	0	0
K	Aqr	-	Aqr	Aqr	Aqr	Aqr	Aqr	Aqr	Per	Aqr	Aqr	Aqr	Aqr	Inv	Aqr	Aqr	0	1	0	0	0	15	0
Mg	Per	Per	Inv	Inv	Per	Per	Per	Per	Per	s	Per	Per	Per	Per	Per	Per	13	0	2	0	1	0	0
Na	Per	Per	Per	Per	Per	Per	Per	Per	Per	Per	Per	Per	Per	Per	Per	Per	16	0	0	0	0	0	0
S	Per	Per	Per	Per	Inv	Inv	Per	Per	Per	Per	Per	Per	Per	Aqr	Per	Per	13	1	2	0	0	0	0
As	Per	Per	-	-	-	-	Per	Per	Per	-	a	Aqr	Per	Per	Per	a	8	1	0	0	0	2	5
Cd	Per	s	Per	-	-	ox	s	s	Per	-	Per	Per	Per	-	Per	-	7	0	0	1	3	0	5
Hg	Aqr	Aqr	Inv	a	Per	ox	Aqr	Aqr	Aqr	Aqr	a	a	Aqr	Aqr	a	s	1	8	1	1	1	4	0
Ni	Per	Per	Per	-	Per	Per	Per	Inv	Per	Per	Inv	Per	Inv	Per	Per	Inv	11	0	4	0	0	0	1
Pb	Per	Per	Per	Per	Per	Per	Per	Per	Per	Per	Per	Per	Per	Per	Per	a	15	0	0	0	0	1	0
Tl	-	-	-	-	-	-	Per	Per	Per	-	-	-	-	-	Per	-	4	0	0	0	0	0	12
U	a	a	Per	-	-	a	a	a	Per	Per	Per	Per	a	a	Per	Per	7	0	0	0	0	7	2
Zn	Per	Per	Inv	Inv	-	Per	Per	Per	Per	Per	-	-	Per	-	Per	-	9	0	2	0	0	0	5
Per	10	9	6	3	7	7	10	9	12	7	8	8	9	7	12	5	Per	$HClO_4/HNO_3/HF$					
Aqr	1	1	0	0	0	0	1	1	1	1	0	1	1	2	1	0	Aqr	Aqua regia					
Inv	0	0	5	4	1	1	0	1	0	0	1	0	1	0	0	1	Inv	Inverse aqua regia					
ox	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	ox	H_2O_2/HNO_3					
s	0	1	0	0	0	0	1	1	0	2	0	1	0	0	0	1	s	$H_2SO_4/H_2O_2/HNO_3$					
a	2	2	1	2	1	2	2	2	1	1	3	2	2	2	1	3	a	NaOH					
-	1	1	2	5	5	2	0	0	0	3	2	2	1	3	0	4	-	Below LOQ					

1.4.3 Determination of Chromium (VI)

The element chromium is ubiquitously present in different minerals. It is vital for many organisms. Chromium can have different oxidation (II-VI) stages but exists in the natural environment mainly as chromium III or VI. Trivalent chromium is present mostly in form of natural minerals. In contrast, hexavalent chromium is mainly of anthropogenic origin and seldom of natural origin (Stollenwerk 1985)(Bartlett 1988). Chromium is predominantly used in the steel industries (ca. 93.7 %) but also in the chemical industries in catalysts, oxidative agents, dyes, wood protectives, tanning agent and as lining material for pyrometallurgical applications. The environmental impact of chromium strongly depends on its oxidation stage. In contrast to the micronutrient Cr(III), Cr(VI) has a high acute toxicity and is declared carcinogenic (Zhitkovich 2011). Due to the high water solubility of many Cr(VI) compounds, it is often also very mobile in the environment.

The total chromium content in the investigated materials was in a wide range between 3.5 to 279 mg/kg. The determination of the Cr(VI) mass fraction after DIN EN 15192 was possible for all matrices and the results reached from 0.02 mg/kg (0.02 % of total Cr) to 12.3 mg/kg (13 % of total Cr). According to the German fertilizer ordinance (DüMV) two samples exceeded the limit value of 2 mg/kg.

For quality control spiking experiments were carried out with Cr(III) and Cr(VI) compounds. The quality control by spiking with Cr(III) showed that no undesired oxidation from Cr(III) to Cr(VI) takes place during extraction. In most cases spiking with Cr(VI) compounds (water soluble and hardly water soluble) led to satisfying recoveries indicating that no undesired reduction of Cr(VI) takes place during extraction. However, samples with organic matter (sewage sludge and precipitated struvite with residues of sludge) or sewage sludge ashes originating from incomplete incineration processes clearly showed underestimations due to reduction of Cr(VI) during the extraction procedure. Thus, the quality control by Cr(VI) spiking failed in these cases. Also the potentially present Cr(VI) in the samples would be reduced during the extraction procedure by the matrix. Consequently, the determined Cr(VI) mass fractions cannot be interpreted and accordingly the method for Cr(VI) determination is not applicable to those matrices containing either organic or inorganic reductives as it was this case. It was possible to apply successfully the quality control by Cr(VI) spiking with satisfying recoveries when the sewage sludge ashes were oxidatively post-treated at 1000°C. For the matrices with high organic fractions (e.g. sewage sludge) a satisfying recovery of spiked Cr(VI) was found when the extraction temperature was decreased from 92.5°C to 80°C. Further investigations are required to find out if the method (DIN 15192) could be optimized by such a measure. This would be of special interest in view of the background of the amendment of the sewage sludge ordinance.