COMPARISON OF DIGESTION METHODS TO DETERMINE HEAVY METALS IN FERTILIZERS(1)

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SUMMARY

The lack of a standard method to regulate heavy metal determination in Brazilian fertilizers and the subsequent use of several digestion methods have produced variations in the results, hampering interpretation. Thus, the aim of this study was to compare the effectiveness of three digestion methods for determination of metals such as Cd, Ni, Pb, and Cr in fertilizers. Samples of 45 fertilizers marketed in northeastern Brazil were used. A fertilizer sample with heavy metal contents certified by the US National Institute of Standards and Technology (NIST) was used as control. The following fertilizers were tested: rock phosphate; organo-mineral fertilizer with rock phosphate; single superphosphate; triple superphosphate; mixed N-P-K fertilizer; and fertilizer with micronutrients. The substances were digested according to the method recommended by the Ministry for Agriculture, Livestock and Supply of Brazil (MAPA) and by the two methods 3051A and 3052 of the United States Environmental Protection Agency (USEPA). By the USEPA method 3052, higher portions of the less soluble metals such as Ni and Pb were recovered, indicating that the conventional digestion methods for fertilizers underestimate the total amount of these elements. The results of the USEPA method 3051A were very similar to those of the method currently used in Brazil (Brasil, 2006). The latter is preferable, in view of the lower cost requirement for acids, a shorter digestion period and greater reproducibility.

Index terms: soil contamination, soil pollution, chemical extraction.

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RESUMO: *COMPARAÇÃO DE MÉTODOS DE DIGESTÃO PARA METAIS PESADOS EM FERTILIZANTES*

A ausência de normatização de um método-padrão para determinar os metais pesados em fertilizantes no Brasil e a consequente utilização de diversos métodos de digestão têm provocado variações nos resultados, dificultando a sua interpretação. Nesse contexto, o objetivo deste trabalho foi comparar a eficiência de três métodos de digestão de fertilizantes para delimitar os metais Cd, Ni, Pb e Cr. Foram utilizadas 45 amostras de fertilizantes comercializados no nordeste do Brasil, além de uma amostra de fertilizante com teores de metais certificados pelo National Institute of Standards and Technology (NIST), incluindo fosfato natural, fertilizante organomineral com fosfato natural, superfosfato simples, superfosfato triplo, fertilizante misto e fertilizante com micronutrientes, que foram digeridos pelos métodos do Ministério da Agricultura, Pecuária e Abastecimento (MAPA) e da Agência Americana de Proteção Ambiental (USEPA): 3051A e 3052. Os resultados demonstraram que o método USEPA 3052 apresentou maiores recuperações para metais menos solúveis, como Ni e Pb, evidenciando que os teores totais desses elementos são subestimados pelos métodos convencionais de digestão para fertilizantes. O método USEPA 3051A evidenciou resultados muito semelhantes ao método atualmente em uso no Brasil (Brasil, 2006), sendo preferido seu uso em razão da diminuição dos custos com ácidos, do menor tempo de digestão e da maior reprodutibilidade.

Termos de indexação: contaminação de solos, poluição de solos, extrações químicas.

INTRODUCTION

The increasing application of fertilizers to meet the crops' nutritional requirements has caused the annual addition of hundreds of tons of heavy metals to the soil, due to the impurities present in these substances (Lottermoser, 2009). Commercial fertilizers contain an extremely varied range of products from different raw materials, resulting in various types of matrices (Kane & Hall Jr., 2006) that are accessed differently by chemical extractions. In this context, the use of effective methods for monitoring these metals in fertilizers is very important for the assessment of potential risks for soils.

International laws that regulate metal content in phosphate fertilizers vary widely. For example, the maximum levels of Cd and Pb in phosphate fertilizers are 10 and 61 mg kg^{-1}, respectively, in the United States (Westfall et al., 2005), 8 and 100 mg kg^{-1} in Japan and China (AFPC, 2012) and 4 and 20 mg kg^{-1} per percentage point (%) of P_2O_5 in Brazil (Brasil, 2006). The Brazilian Ministry of Agriculture, Livestock and Food Supply (MAPA), by Normative Regulation No. 27/2006, determines the maximum allowed limit of Cd, Pb, Ni and Cr in mineral and organic fertilizers in the country (Brasil, 2006). However, due to the lack of a standard method for the extraction of heavy metals from fertilizers, various methods of acid digestion have been used instead. These methods can use concentrated hydrochloric acid (HCl) in an open system (Brasil, 2006) or hydrochloric and nitric acids in closed (microwave) systems (Campos et al., 2005).

The different methods for recovering metals from fertilizers produce highly variable results for a same sample (Kane & Hall Jr., 2006), making comparisons very difficult. Campos et al. (2005) compared two methods for heavy metal determination in fertilizers, indicated by the Normative Regulation No. 24/2007, and observed that greater quantities of Pb were extracted by USEPA method 3051A, whereas more Cd was recovered by USEPA 3050B.

The method proposed by MAPA (Brasil, 2006) is considered a conventional procedure because it is conducted in an open system where metals are extracted under heating (hot plate) in the presence of concentrated HCl. Despite being widely used, this method poses serious health risks to laboratory technicians for releasing toxic gases, aside from not being very efficient, due to the loss of the most volatile components (Nieuwenhuize et al., 1991). In addition, the absence of essential analytical details, such as the temperature of the hot plate to be maintained and digestion time, also contributes to variations and uncertainties. On the other hand, the USEPA method 3051A mixes hydrochloric and nitric acids, thus improving the recovery of some metals, such as Ag, Al, Fe, and Sb (USEPA, 1997). It is also carried out in a microwave oven, providing higher temperature and pressure and making the digestion process faster, safer and more efficient, in addition to reducing the loss of volatile components and acid costs.

The objective of this study was to compare the effectiveness of three digestion methods to determine Cd, Ni, Pb, and Cr in 45 samples of mineral fertilizers. This work also aimed to provide supporting information for the standardization of analytical methods for metal determination in fertilizers by MAPA.

MATERIAL AND METHODS

The study was conducted using 45 samples of fertilizers sold in northeastern Brazil, including rock phosphate, organo-mineral fertilizer with rock phosphate, single superphosphate, triple superphosphate, mixed fertilizer (NPK) and micronutrient fertilizer, all supplied by the National Agricultural Laboratory of the Ministry for Agriculture, Livestock and Supply of Brazil (MAPA) in Pernambuco (LANAGRO-PE) (Table 1). The samples were ground in an agate mortar and sieved (0.3-mm stainless steel mesh) (ABNT no. 50) to avoid contamination.

Three digestion methods for fertilizers were evaluated, described below. All digestions were performed in duplicate:

MAPA (Brasil, 2006): 1.0 g of each sample was transferred to Teflon beakers and 10 mL of concentrated HCl were added. The solution was heated on a hot plate and boiled until complete evaporation of the acid, but without burning the residue. Subsequently, 20 mL of HCl 2 mol L^{-1} were added to the residue, which was heated to boiling on the hot plate.

USEPA 3051A (USEPA, 1998): 0.5 g of each sample was transferred to Teflon tubes, adding 9 mL HNO_3 and 3 mL HCl. The tubes were maintained in a closed system (Mars Xpress microwave oven), then a temperature ramp to 175 °C for 8' 40". This temperature was maintained for a further 4' 30".

USEPA 3052 (USEPA, 1996): 0.5 g of each sample was placed in Teflon tubes, adding 9 mL HNO_3 and 3 mL HF. The tubes were maintained in a closed system (Mars Xpress microwave oven) for 5' 30” to reach 180 °C. This temperature was maintained for a further 4' 30”.

After digestion, the extracts were transferred to certified 25-mL flasks (NBR ISO/IEC), which were filled with ultrapure water (Direct System - Q Millipore) and the content filtered through slow paper filter (Macherey Nagel®). High purity acids (Merck PA) were used. Quality control analysis was carried out using a sample of multi- nutrient fertilizer with metal levels certified (SRM 695) by the National Institute of Standards and Technology (NIST) and multi-nutrient solutions (spikes) with known concentrations of the analyzed metals, in addition to blank solutions. The spikes were prepared using 1,000 mg L^{-1} stock solutions (Titrisol®, Merck) with concentration equal to the midpoint of the calibration curve, for each metal. The controls (SRM 695, spike and blank) were introduced after every 20 samples analyzed and subjected to the same digestion and metal determination procedures. Calibration curves for determining the metals were prepared from standard Titrisol® (Merck), and the samples were only

Table 1. Analyzed fertilizers

Sample number	Fertilizer	Sample number	Fertilizer
1	12-24-18 + 3 % S	24	Single superphosphate
2	6-24-18 + 4 % Ca + 5 % S	25	Single superphosphate
3	10-10-10 + 4 % Ca + 12 % S	26	Single superphosphate
4	4-14-8 + 12.9 % Ca 11.3 % S	27	Single superphosphate
5	6-24-12 + 6.9 Ca + 6.8 % S	28	Single superphosphate
6	10-10-10 + 6.19 % Ca + 14.2 % S	29	Single superphosphate
7	20-10-20 + 3.4 % Ca	30	Single superphosphate
8	4-14-8 + micro	31	Triple superphosphate
9	12-24-18 + micro	32	Triple superphosphate
10	16-16-16	33	Organo-mineral (1-00-00)
11	16-16-16	34	Organo-mineral (1-14-11)
12	16-16-16	35	Organo-mineral (13-00-5)
13	20-10-20	36	Organo-mineral (10-00-2)
14	20-10-20	37	Organo-mineral with rock phosphate
15	10-10-10	38	Organo-mineral with rock phosphate
16	6-24-12	39	Organo-mineral with rock phosphate
17	Single superphosphate	40	Organo-mineral with rock phosphate
18	Single superphosphate	41	Rock phosphate
19	Single superphosphate	42	Rock phosphate
20	Single superphosphate	43	Rock phosphate
21	Single superphosphate	44	Rock phosphate
22	Single superphosphate	45	Rock phosphate
23	Single superphosphate		

analyzed when the R^2 of the calibration curve was greater than 0.999. Calibration was checked initially and then after every 20 samples analyzed; in case of deviation of more than 10 %, the equipment was recalibrated.

The Cd, Cr, Ni and Pb in the extracts was determined by optical emission spectrometry (ICP-OES/Optima 7000, Perkin Elmer) with dual viewing mode (axial and radial) and solid-state detector with introduction system by an autosampler (PerkinElmer, Model AS 90 Plus). The results were subjected to descriptive statistics, the Pearson product-moment correlation between the metals in each method and analysis of variance. The Tukey's test at 5 % probability was used to compare the means (SAS Learning Edition version 2.0).

RESULTS AND DISCUSSION

The highest rates of average metal recovery from NIST SRM 695 were obtained by USEPA 3052 (Table 2), due to HF addition, which solubilizes the metals contained in environmentally inaccessible fractions, thus recovering a higher metal content. It is noteworthy that the metal content of the certified material is determined by non-destructive methods, such as neutron activation, or by methods involving the complete dissolution of the sample (USEPA, 1996), whereas the MAPA method and USEPA 3051A determine the environmentally available or pseudo total content.

For Pb and Ni, the differences among recovery rates of the methods were highest (> 20 %) indicating a stronger association of these elements in the certified sample to fractions not accessed by the methods traditionally used to determine metals in fertilizers. The association of the metals Cd and Cr to the more recalcitrant fractions was the weakest, with 8 and 11 % higher contents, respectively, by USEPA 3052 (Table 2).

The results of metal recovery by NIST SRM 695 were similar by the methods of MAPA and USEPA 3051A (Table 2), demonstrating that both can be used to extract Cr and Cd from the certified sample. The low Cr recoveries by pseudo total methods corroborate Kane & Hall Jr. (2006), who determined metals in NIST SRM 695 in various laboratories and found a low average recovery of Cr (73 %) when using concentrated HNO_3 as digestion procedure, in a closed microwave system.

In relation to the quality control of analyses by spike recovery, the mean heavy metal recoveries were very good (between 96 and 110 %), for all metals in all methods. These results rule out possible metal loss by volatilization during sample digestion in the open system (Table 3).

The mean Pb and Ni contents in the fertilizers were significantly higher when extracted by USEPA 3052 (Figure 1), indicating that considerable amounts

Table 2. Cadmium, nickel, lead, and chromium recoveries in NIST SRM 695, certified values and means of the found values

Method	Certified value	Found value	SD(1)	Recovery
	mg kg^{-1}		%	
		Cd		
MAPA		15.47	1.98	92.63
3051A	16.7	15.37	0.98	92.03
3052		16.76	1.63	100.3
		Ni		
MAPA		85.16	5.56	64.00
3051A	133	82.73	4.38	62.20
3052		115.80	12.77	87.06
		Pb		
MAPA		188.00	12.48	73.43
3051A	256	195.40	10.51	76.32
3052		227.00	18.40	97.42
		Cr		
MAPA		165.60	16.41	69.57
3051A	238	167.20	9.23	70.25
3052		192.80	11.87	81.00

(1) Standard deviation.

Table 3. Mean recoveries for cadmium, nickel, lead, and chromium in spikes

Method	Certified value	Found value	SD(1)	Recovery
	mg kg^{-1}		%	
		Cd		
MAPA		1.28	0.16	106
3051A	1.20	1.20	0.14	100
3052		1.20	0.05	100
		Ni		
MAPA		1.30	0.17	108
3051A	1.20	1.20	0.11	100
3052		1.25	0.07	104
		Pb		
MAPA		6.41	1.00	107
3051A	6.00	6.04	0.58	100
3052		6.46	0.49	107
		Cr		
MAPA		3.31	0.52	110
3051A	3.00	3.28	0.33	109
3052		2.88	0.01	96

(1) Standard deviation.

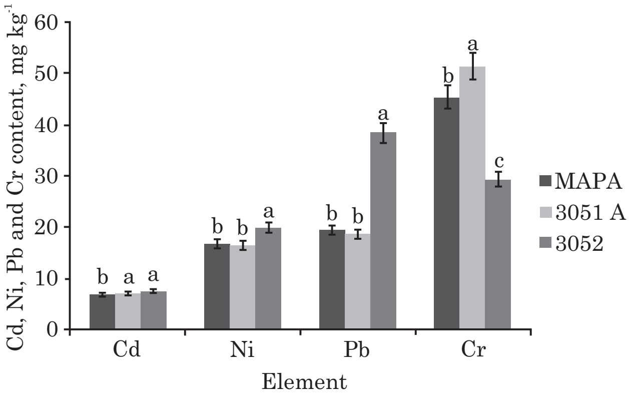

Figure 1. Mean content and standard deviation for metals extracted by the MAPA method, USEPA method 3051A and USEPA method 3052 in 45 fertilizer samples. Means with the same letter are significantly identical by the Tukey's test ($p<0.05$).

of these metals are associated to more recalcitrant fractions of the fertilizers. Mean Cd concentrations extracted by USEPA 3051A were statistically identical to those obtained by USEPA 3052, indicating a higher solubility of this metal and lower quantity linked to the environmentally inaccessible fractions. These results corroborate the findings of Bizarro et al. (2008), who reported a positive correlation between two methods for Cd extraction from fertilizers: by nitryl perchlorate, which causes the complete dissolution of the sample, and USEPA 3050B, which is less aggressive and extracts only environmentally available fractions. Gonçalves et al. (2008), when analyzing six phosphate fertilizers, also reported that the Cd concentrations extracted by nitryl perchlorate were fully bioavailable. Due to its high solubility in both soils and fertilizers, Cd is one of the most investigated metals in studies on soil contamination by fertilizers (Taylor, 1997; Mendes et al., 2006; Nziguheba & Smolder, 2008; Freitas et al., 2009; Jiao et al., 2012).

The Cr content extracted from fertilizer samples was significantly lower by USEPA 3052 than by pseudo total methods (Figure 1), because Cr(III) forms inorganic ligand complexes with fluoride (Calder, 1988). In addition, Kane & Hall Jr. (2006) reported that some Cr forms are more difficult to solubilize in the absence of HCI during digestion, resulting in a greater range of values for this element. There was no significant difference between the mean concentrations of Ni and Pb extracted by USEPA 3051A and the MAPA method, but the mean Cd and Cr recoveries were significantly higher when extracted by USEPA 3051A (Figure 1). In this context, USEPA 3051A is indicated in studies involving a wide range of matrices and the analysis of various metals. Nemati et al. (2009) also observed a lower Cd recovery from sewage sludge when digested on a hot plate, in relation to the closed system, attributing these results to higher losses by volatilization and oxidation. Campos et al. (2005) compared metal recovery from mineral fertilizers, and found no significant difference between the open-system methods USEPA 3051A and 3050B for Ni extraction.

Extraction with strong acids (HNO_3 and/or HCl) by the methods of MAPA and USEPA 3051A aims to determine the potential availability and mobility of heavy metals in the environment. The MAPA was highly correlated (0.99, $p<0.01$) with USEPA 3051A for all metals tested, indicating that both methods may be appropriate for determining environmentally available levels of these metals. However, USEPA 3051A may be the best alternative for the extraction of the analyzed metals from fertilizers, due to the reduced risk of toxic gas release in the laboratory and lower element loss by volatilization and drying. Furthermore, USEPA 3051A requires less acids and a shorter digestion time for metal recovery. These results corroborate observations of Campos et al. (2005), who reported that USEPA 3051A and conventional methods are viable to determine heavy metals in fertilizers. These authors also highlighted the microwave oven method as more advantageous.

CONCLUSIONS

1. Although the USEPA method 3052 generally promoted a more complete digestion, it is not recommended for regulatory purposes by the Brazilian legislation, for extracting environmentally inaccessible metal concentrations from soil and fertilizer samples, present in more recalcitrant fractions.

2. The method currently used in Brazil (Brasil, 2006) and USEPA method 3051A produced very similar results, the latter being recommended in studies involving a large range of matrices and analyses of various metals. For the method USEPA 3051A, costs with acids are lower and the digestion time shorter, aside from its better reproducibility. However, in laboratories where no microwave oven for digestion is available, the open-system method MAPA is suitable for the analysis of the studied metals.

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