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Determination of inorganic contaminants in glue by inductively coupled argon plasma optical emission spectrometry

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ABSTRACT

A closed vessel method using a microwave oven was developed for the determination of As, B, Ba, Bi, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Se, Sn and Sb by Inductively Coupled Argon Plasma Optical Emission Spectrometry (ICP OES). The method was applied to samples of polyvinyl acetate-based glue in water emulsions. Parameters such as wavelength, nebulization pressure and RF power were optimized and the residual acidity after the digestion process was determined. The addition of internal standards was evaluated and the accuracy of the proposed method was verified with addition and recovery experiments and also with certified reference materials, achieving good results. Using a nebulization flow rate of 0.73 L min^{-1} and a RF power of 1200 W it was possible to obtain adequate values for limit of detection and limit of quantification as well as recovery values in the range of 80–106%, for all the analytes. The analysis of coloured glue samples (white, black, blue, yellow, red and green), widely used by children, showed no contamination by the elements studied.

1. Introduction

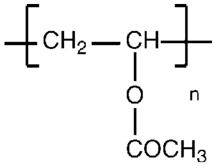
Many of the chemical and physical properties of polymers, such as thermostability, chemical stability, flame-retardation, dying ability, and antistatic properties, are often changed by the use of additives during polymer synthesis [1]. Some of these additives contain inorganic ions in their composition and, considering parallel effects that they may introduce into the polymers, the ability to quantify these ions is an important task for industries that need to analyze dozens of these products.

Several researchers have been interested in developing procedures aiming at the optimization of complete sample digestion leading to reliable and fast methods without loss of analyte. Besecker et al. [2] described a simple, closed-vessel microwave digestion method for the determination of metals by inductively coupled plasma emission spectrometry in polyethylene, polypropylene, and polystyrene using nitric acid under high pressure (75 bar), obtaining recoveries in the range of 90–100%. Eilola and Peramaki [3] carried out a vapor-phase digestion for polyethylene samples using sulfuric acid, nitric acid and hydrogen peroxide in a focused microwave system.

Some other authors [4,5] have described the development of methods for the determination of inorganic ions (lead, mercury, chromium and cadmium) in food-packaging materials, especially those based in polymeric materials. Trace metal contamination in such materials is a potential problem because these elements might migrate into food during storage. According to the EU 94/62/EC directive the maximum limits of total heavy metals (Hg, Cd, Pb, Cr) that may be present in packaging materials is 100 mg kg^{-1} [5].

There are not many papers from the last decade that deal with this subject [6] and additionally there are also only a few certified reference materials that may be used to validate analytical methodologies, but fortunately this field is growing. The most analyzed samples are solid polymers such as polyethylene, polystyrene and polyvinyl chloride, and there are few methodologies for emulsion polymers like polyvinyl acetate (PVAc).

Like most of the vinyl polymers, polyvinyl acetate is commercially prepared by polymerization of monomeric vinyl acetate in the presence of a peroxide catalyst (hydrogen peroxide or organic peroxides) in a bulk or emulsion polymerization according to the formula [7]:



$$\left[CH_2 - CH(OCOCH_3) \right]_n$$

Polyvinyl acetate finds numerous applications in the manufacture of emulsion paints, varnishes and adhesives [8]. In many countries it has been used as a masticatory substance in chewing gum base [9]. It is also used in cosmetics as a binder, emulsion stabilizer, and hair fixative [10]. Another application of this material is

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Table 1
Instrument operating conditions for the determination of metals in polyvinyl acetate.

Radio frequency power (kW)	1.2	
Plasma gas flow rate ($L\,min^{-1}$)	15	
Auxiliary argon flow rate ($L\,min^{-1}$)	1.5	
Nebulizer pressure (kPa)	210[a]	
Replicate read time (s)	5	
Pump rate (rpm)	15[b]	
Replicates	3	
Wavelengths (nm)	As(I) 193.696	Fe(II) 238.204
	B(I) 249.772	Hg(I) 184.887
	Ba(II) 585.367	Ni(II) 230.299
	Bi(I) 206.163	Pb(II) 220.353
	Cd(II) 226.502	Sb(I) 206.834
	Cr(II) 267.716	Se(I) 203.985
	Cu(I) 327.395	Sn(I) 283.998
Sample uptake delay (s)	40	
Pump rate (rpm)	15	
Rinse time (s)	10	
Replicates	3	
Sampler	SPS3	
Chamber	Cyclonic	
Nebulizer	Seaspray	
Torch	High solids (injector tube 2.4 mm)	

[a] This instrument is not fitted with a mass flow controller, thus the nebulizer is set using pressure. A pressure of 210 kPa is about $0.73\ mL\,min^{-1}$.

[b] The sample uptake rate is set adjusting the peristaltic pump speed.

Table 2
Microwave digestion program for polyvinyl acetate.

T (min)	T (°C)	E (W)
7	120	400
5	120	400
5	180	800
10	240	800
30	240	800

in glues, especially those used by children. They have a creamy consistency and, after drying, show transparency and offer permanent adherence but are not water resistant. The most common glues are white but they can also be coloured.

The additives used to give colour to the polymers can be classified as pigments and dyes. The main differences between them are related to particle size and solubility in the medium in which they are inserted. Pigments have, in general, larger particle sizes and are insoluble in the polymer, while dyes are soluble in polymer molecules [11].

The determination of metals in polyvinyl acetate has only recently been investigated [12], although this polymer is widely used in different kinds of materials in daily used.

The aim of the present work was to determine some inorganic ions (As, B, Ba, Bi, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Sb, Se and Sn) in coloured glue samples. The samples were submitted to a microwave treatment and the ions were determined by inductively coupled plasma optical emission spectrometry (ICP OES) after validation of the proposed method using optimized instrumental parameters.

2. Experimental

2.1. Instrumentation

All the measurements were made with a Varian 720 ES (axial view) inductively coupled plasma optical emission spectrometer (ICP OES) equipped with a solid-state charge-coupled device detector (CCD), a peristaltic pump and a “Seaspray” nebulizer coupled to a cyclonic nebulization chamber. A CCI (Cooled Cone Interface) was set with an argon flow rate of $3\ L\,min^{-1}$. The optimised operational conditions of the spectrometer are presented in Table 1. Background correction was done using two points method.

For sample treatment a microwave oven (Milestone ETHOS TC), equipped with pressure sensor (up to 50 bar), temperature sensor and TFM flasks (temperature up to 260 °C and pressure up to 100 bar) were used.

The investigation of residual acidity used a potentiometric titrator, Metrohm 682, equipped with a glass electrode (Metrohm, ref. 6,0233,100), using $0.1\ mol\,L^{-1}$ NaOH solution as titrant.

A Metrohm ionic chromatograph equipped with a Metrosep A Supp 5 – 150/4.0 mm column and a Metrosep A Supp 5 4/5 guard column and a conductivity detector was also used.

Solutions of $3\ mmol\,L^{-1}$ Na_2CO_3 and $1\ mmol\,L^{-1}$ $NaHCO_3$ were used as eluent (flow rate $0.7\ mL\,min^{-1}$). Injection used a $10\ \mu L$ loop and suppression (deionized water and sulfuric acid $100\ mmol\,L^{-1}$).

2.2. Solutions and reagents

Pure argon (99.996%, White Martins, SP, Brazil) was used. All the glassware used was cleaned with dilute nitric acid (10%, v/v) and then with deionized water (MilliQ system, $18.2\ M\Omega\,cm$).

The 70% (w/w) nitric acid was from Merck. The stock ICP solutions ($1000\ mg\,L^{-1}$) were from Chemis or TecLab with certified concentrations. All working standards were matrix matched and prepared in class A volumetric flasks. All other reagents were at least p.a. grade.

The certified reference materials (CRMs) BCR 680 and BCR 681 (high density polyethylene and low density polyethylene), which have the following additives: As_2O_3, Green 36, ZnS/CdS, Green 7, Cr_2O_3, $PbCrO_4/PbSO_4$, HgS, Sb_2O_3, SnO_2, were also analyzed.

The samples used for the parameters optimization in this work were non-ionic water emulsions of polyvinyl acetate with additives and polyvinyl alcohol. The pH was between 4 and 5, the viscosity between 16.000 and 22.000 mPa s at 25 °C, and the solid content was 51–53%.

Commercial samples of glues with different colours were analized with the proposed method.

Scandium ($1\ mg\,L^{-1}$) and yttrium ($1\ mg\,L^{-1}$) were added to the reference solutions and glue samples as internal standards.

2.3. Procedure

Samples were weighed (about 0.5 g of glue or 0.2 g of certified reference materials) into a High Pressure TFM vessel together with 5 mL of concentrated HNO_3 and 3 mL H_2O. These were treated as described in Table 2. After cooling, the solutions were diluted to 25 mL with water and the emission intensity was measured against an analytical curve.

3. Results and discussion

3.1. Wavelength selection

Three different wavelengths for each analyte were evaluated considering the linearity of analytical curve and the signal to background ratio (SBR) (ratio between the analyte intensity emission and the blank emission) [13,14]. The best results were obtained using the wavelengths described in Table 1.

3.2. Pressure nebulizer and radio frequency power

For the optimization of these parameters the SBR for the Mn emission line at 257.610 nm [15] and the robustness, calculated as

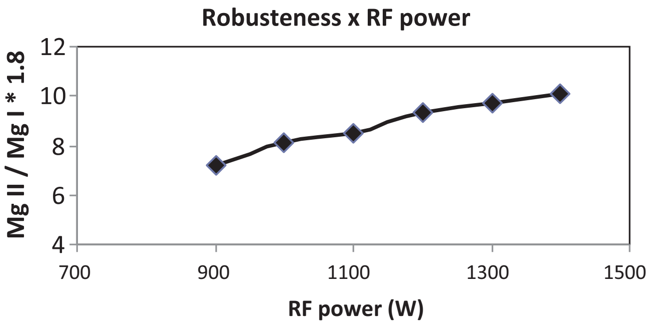


Fig. 1. Effect of nebulization flow rate on robustness.

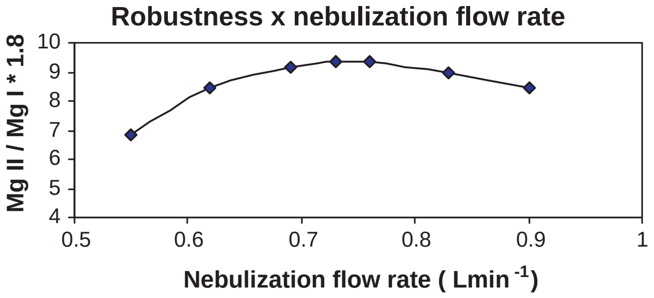


Fig. 2. Effect of radio frequency power on robustness.

the ratio between the ion emission line of Mg(II) (280,270 nm) and the atomic emission line of Mg(I) (285,213 nm) [14], were considered. Robustness represents the efficiency of energy transfer and the response of plasma to changes in atomization and excitation conditions and to the chemical composition of the aspirated solution [16]. The results obtained for these parameters were shown in Figs. 1 and 2.

The MgII/MgI ratio decreases slowly for nebulization flow rates higher than 0.70 L min^{-1} and increases with the radio frequency power. Silva et al. [16] demonstrated that the ratio (MgII/MgI) must be multiplied by 1.8 to correct response intensities when an Echelle grating and a solid-state detector are used.

The best results for robustness and SBR were obtained for a nebulization flow rate of 0.73 L min^{-1} (210 kPa) and a RF power of 1200 W.

3.3. *Internal standard*

Internal standardization is used to compensate the effects of changes in intensity due to the sample matrix, thereby enhancing the precision and accuracy of the determination.The residual acidity after microwave digestion (final dilution to 25 mL) was determined by potentiometric titration. The results, expressed in nitric acid, indicated an average value of 14.9%. According to Brenner [17] the interference effects due to an acid matrix are shown in the following ways: (a) an increase in the viscosity that affect aerosol generation and sample introduction; (b) changes in atomization and excitation conditions; (c) changes in the aerosol droplet size distribution. The decrease in the analytical signal in the presence of HCl or HNO_3 concentrations higher than 10% is more pronounced in an axial system, but the use of internal standards may improve signal recovery.

In this work scandium and yttrium, at concentrations of 1 mg L^{-1}, were investigated as internal standards. Table 3 shows the results obtained with the use of Y and Sc as internal standards, compared with results obtained without addition of internal standards (without IS).

The results showed no significant difference (95% confidence level) in the analytical signals in the presence of Y or Sc. A statistical evaluation was made by comparing the confidence intervals between the results for each analyte and the *P*-value from ANOVA. The differences obtained are within the RSD range, considering recovery values obtained in the presence or absence of internal standard. One possible explanation is that, when using the plasma under robust conditions [17], matrix effects (such as the presence of mineral acids) are minimized. Considering the results obtained, it was concluded that the use of internal standard is not necessary.

3.4. *Residual acidity*

As the thermal degradation of PVAc samples leads to the formation of acetic acid [18], according to the following reaction, a certain contribution of this compound to the acid remaining after digestion by microwaves is expected.

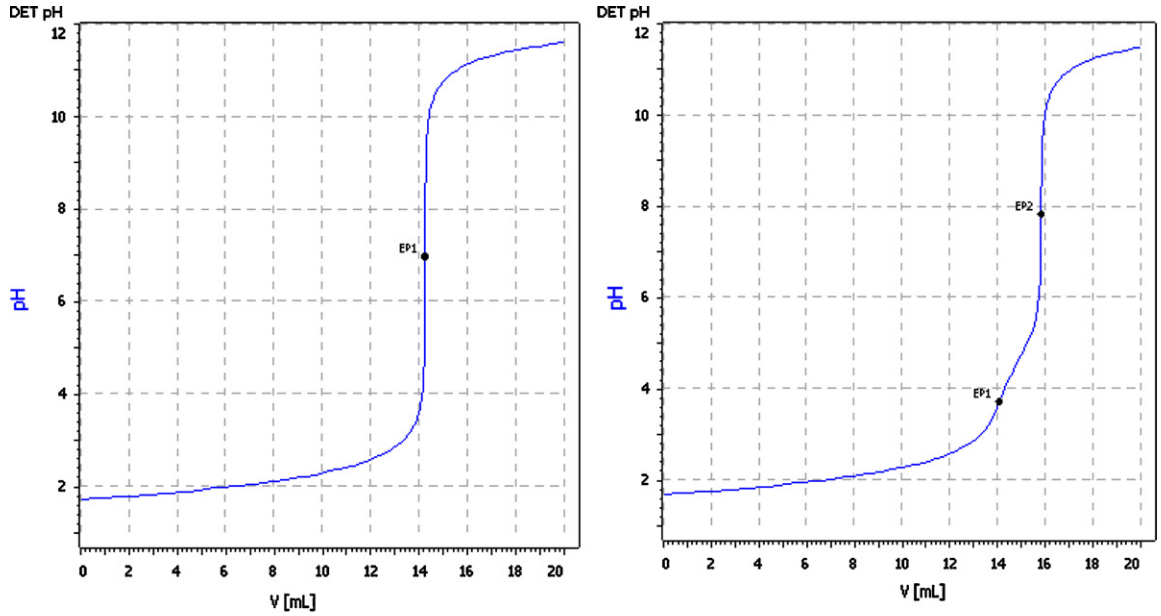
$$(\text{–}CH_2\text{–}CH\text{–}OOC\text{–}CH_3)_n \xrightarrow{\Delta} CH_3COOH + CH_2{=}CH_2$$

The hypothesis that the acetic acid (HAc) generated during PVAc degradation remains as a residual acidity in the solution was verified by potentiometric titration and ion chromatographic analysis of a digested solution.

Fig. 3 shows titration curves obtained for standard solutions of nitric acid (Fig. 3a) and nitric acid + acetic acid (Fig. 3b) using standardized 0.1 mol L^{-1} NaOH solution, while the curve for the digested sample is shown in Fig. 4. Nitric acid, being the stronger acid, is neutralized at a pH lower than that for acetic acid (the first inflection in Fig. 3b is related to HNO_3 neutralization and the second one refers to HAc neutralization). This profile was verified for different acidity conditions and the end points were confirmed with

Table 3
Recovery values obtained in the presence and absence of internal standards (IS).

Element	Without IS		With Sc		With Y	
	RSD	Recovery (%)	RSD	Recovery (%)	RSD	Recovery (%)
As 193,696	1.3	94.6	2.3	92.8	2.3	93.1
B 249,772	1.6	79.6	4.6	77.5	3.9	74.7
Cd 226,502	1.8	94.0	3.6	94.3	3.1	91.7
Cr 267,716	1.8	98.5	3.3	98.7	3.0	97.3
Cu 327,395	1.4	99.2	3.2	98.7	2.5	97.6
Fe 238,204	2.9	106.1	4.3	106.3	4.1	104.1
Hg 184,887	4.5	94.6	10.0	91.9	6.4	94.0
Ni 230,299	1.0	97.8	1.3	97.2	0.5	95.6
Pb 220,353	3.1	92.0	4.7	91.4	4.5	90.0
Sb 206,834	2.8	90.4	5.2	90.7	3.5	86.3
Ba(II) 585,367	1.6	96.9	2.9	97.1	2.2	95.0
Bi(I) 206,163	2.6	98.0	3.6	98.4	3.7	94.4
Se(I) 203,985	3.1	92.2	3.6	91.9	0.8	90.4
Sn(I) 283,998	2.0	89.2	2.9	90.7	2.1	87.9

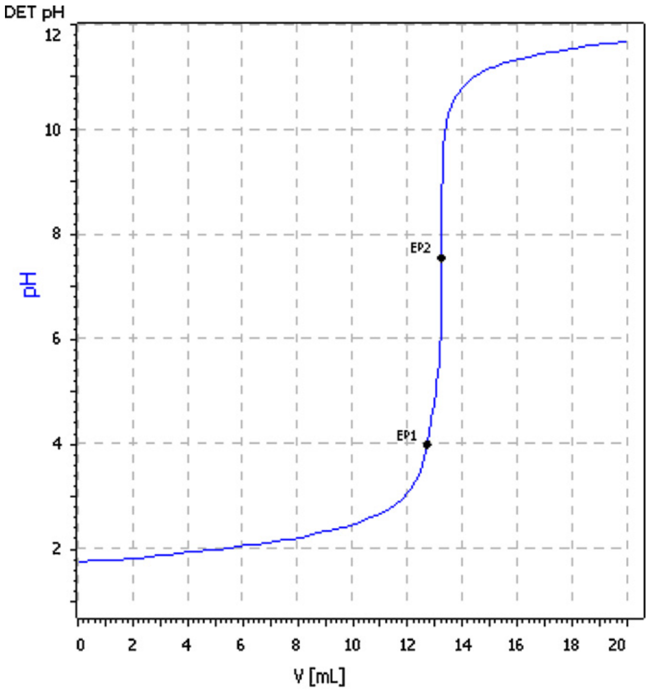


a Standard HNO_3 (8.8% w/w) Dilution volume = 50 mL

b Standard Mixture (HNO_3 8.8% w/w and HAc 1.0% w/w) Dilution volume = 50 mL

Fig. 3. Potentiometric titration for HNO_3 (a) and HNO_3 + HAc (b).

standard addition of nitric or acetic acids to the digested sample, verifying the increase of titrant volume for neutralization for each condition. For a final dilution of 50 mL the digested sample (PVAc) has 0.3% (w/w) of acetic acid and 7.8% (w/w) of nitric acid, as shown in Fig. 4.



Digested sample HNO_3= 7.8% w/w and HAc= 0.3% w/w. (Dilution volume = 50 mL)

Fig. 4. Potentiometric titration for residual acidity of a digested solution of sample (microwave radiation).

After the appropriate dilution of each of the solutions (HNO_3, HAc and sample) a chromatographic analysis by ion chromatography was made in order to determine the anions present in the solutions and to confirm the presence of acetate. Fig. 5 shows the results obtained for each of the solutions, confirming the presence of acetic acid in the digested solution and also the formation of nitrite in the digested solution, which was confirmed by the addition of a known amount of nitrite standard solution. The final content of 0.26% (w/w) for acetate ion is consistent with that obtained by potentiometric titration (0.3%, w/w).

3.5. Analysis of certified reference materials

In this work two certified reference materials, which are polymers of high and low density, were analyzed to confirm the accuracy of the proposed method. Tables 4 and 5 describe the results obtained for the analysis of BCR 680 and BCR 681, which were used because of the similar matrix to the samples (polymer matrix) and also because there is a lack of certified materials for polymeric materials, especially for polyvinyl acetate. The results with these materials are described in Tables 4 and 5, where is possible to note that the determination of Hg for BCR 680 showed a high relative standard deviation (40.8%) and a low recovery value (66%). However, this is not unexpected considering that the certified value (4.64 mg kg^{-1}) is very near the limit of quantification (5.0 mg kg^{-1}).

The determination of Sb was not suitable, possibly due to the form of this element (Sb_2O_3) in the reference sample. In the experiments of addition and recovery, this analyte was added in its soluble form (standard prepared from antimony metal dissolved in 10% (w/v) HCl) and the results were good. Considering that antimony trioxide is only slightly soluble in dilute nitric acid [19], the digestion medium used, most of this oxide was probably retained on the filter paper, during the filtration after microwave digestion, explaining the low recovery values obtained.

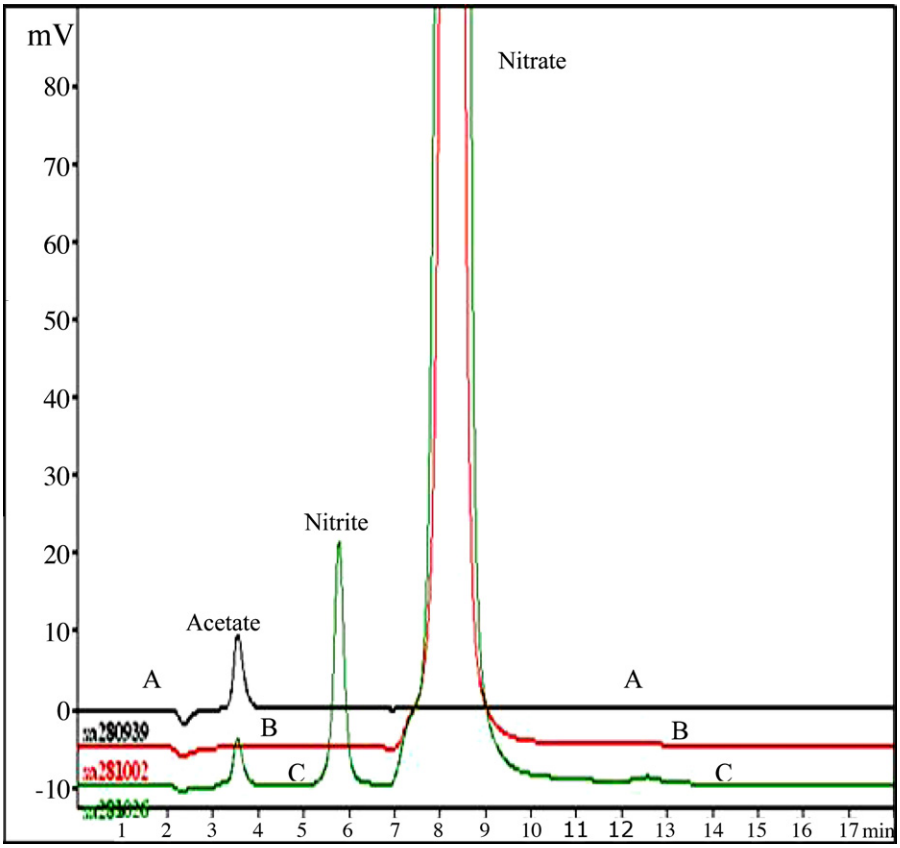


Fig. 5. Chromatograms for HNO_3. HAc and digested solution. A = acetic acid; B = nitric acid; C = digested sample after 100 times dilution.

Table 4
Results obtained for certified reference materials (BCR 680).

Element	Certified value (mg kg^{-1})	Uncertainty (mg kg^{-1})	Result[a] (mg kg^{-1})	Standard deviation (mg kg^{-1})	RSD (%)	Recovery (%)
As	4.1	0.5	3.7	0.59	15.7	91
Cd	19.6	1.4	19.1	0.29	1.5	98
Cr	20.2	1.1	16.0	0.35	2.2	79
Hg	4.64	0.2	3.1	1.25	40.8	66
Pb	13.6	0.5	12.0	0.06	0.5	88
Sb	10.1	1.6	1.0	0.35	34.6	10
S	76	4	80.4	3.80	4.7	106

[a] Average of three determinations.

Table 5
Results obtained for certified reference materials (BCR 681).

Element	Certified value (mg kg^{-1})	Uncertainty (mg kg^{-1})	Result[a] (mg kg^{-1})	Standard deviation (mg kg^{-1})	RSD (%)	Recovery (%)
As	29.1	1.8	27.1	0.57	2.1	93
Cd	137	4	125.1	1.70	1.4	91
Cr	100	5	106.8	1.83	1.7	107
Hg	23.7	0.8	20.1	0.76	3.8	85
Pb	98	6	95.1	1.15	1.2	97
Sb	99	6	2.2	0.70	31.8	2
S	630	40	645.8	8.66	1.3	103

[a] Average of three determinations.

For the other elements the recovery values are satisfactory, especially considering the difference in the composition of the polymers used, polyethylene and polyvinyl acetate.

3.6. Analysis of glue samples

In order to evaluate the presence of inorganic elements in samples of glue, the method was applied to commercially available glue samples. The colours of samples were: white, black, blue, yellow, red and green. The results obtained are shown in Table 6.

It is possible to observe that the majority of the elements were not determined considering the limits of quantification. Iron is present in all the samples and it was also possible to quantify copper in “Blue Az” and “Green Vd” samples, chromium in the “Black AP” sample and nickel in the samples “White TP” and “Blue Az”.

Table 6
Concentration (mg kg^{-1}) obtained for samples of glue (with colouring).

Element	White TP	Black AP	Blue Az	Yellow Am	Red Vm	Green Vd	White AB	LOQ	LOQ × 50
As(I) 193,696	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.15	7.5
B(I) 249,772	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.09	4.5
Ba(II) 585,367	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.005	0.3
Bi(I) 206,163	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.01	0.5
Cd(II) 226,502	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.01	0.5
Cr(I) 267,716	<LOQ	0.3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.003	0.2
Cu(I) 327,395	<LOQ	<LOQ	387.1	<LOQ	<LOQ	163.5	<LOQ	0.07	3.5
Fe(II) 238,204	3.9	3.8	4.7	2.8	3.0	3.6	1.0	0.02	1.0
Hg(I) 184,887	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.04	2.0
Ni(II) 230,299	0.53	<LOQ	1.0	<LOQ	<LOQ	<LOQ	<LOQ	0.01	0.5
Pb(II) 220,353	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.05	2.5

LOQ × 50 = limit of quantification considering the dilution factor.

Among these elements, only chromium has a limit specified by the regulatory agencies [20,21] but the value found is below this limit of 60 mg kg^{-1}. The presence of iron has already been reported in samples of white glue [12]. Considering copper, Saron and Felisberti [11] describes the presence of this metal in the structure of phtalocyanine, an organic colourant that gives blue and green colours to all the polymers, except fluorocarbons and silicon compounds. Nickel may also be present in this kind of compound. Some of the polymers have organic colourants, which do not present metals in their structure.

4. Conclusion

Analysis of glue samples showed values below the LOQ (even considering the LOQ × dilution factor) for most of the analyzed elements, except Fe, Cu and Cr. The concentration of Ni found in white glue is very closed to the LOQ but it was still possible to detect it. For the elements present in the samples, the concentrations found are below those set by regulatory agencies. Considering these results, the use of coloured glue does not represent a health risk.

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