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# Nitrogen, phosphorous and potassium polymeric microparticles: application and validation of analytical methods for determination of a promising fertilizer

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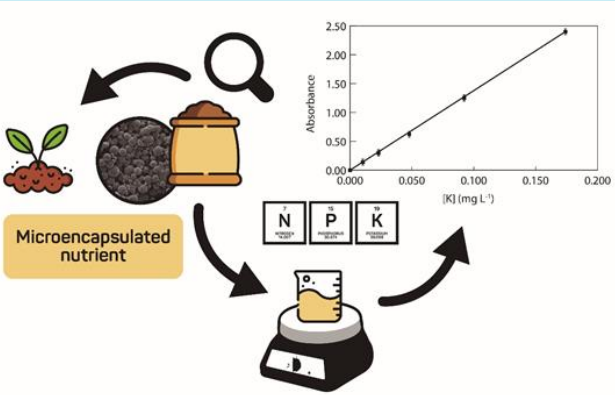
**ABSTRACT:** Traditional analytical methods were applied to microparticles synthesized using a mixture of polymers. The microparticles containing nitrogen, phosphorus and potassium (NPK) were developed for application as a controlled release alternative to traditional fertilizers. Thus, analytical methods for the evaluation of nitrogen, phosphorus and potassium (essential nutrients for plants) in polymeric microparticles were applied and the results validated for this kind of sample. The linearity of the methods was established in the range of 10 to 20 mg $L^{-1}$ for N, 0 to 2 mg $L^{-1}$ for P and 0 to 2.4 mg $L^{-1}$ for K. The relative standard deviation (RSD) of intermediate precision of the method was < 1% and recoveries from 99 to 108% for all nutrients were reached. The method proved to be selective, linear, precise and accurate for quantifying NPK in polymeric microparticles. In this way, it was possible to evaluate the correct nutrient encapsulation capacity in the synthetized polymeric microparticles, which is of fundamental importance since this will directly interfere in the success of the intended fertilization process.




Methods that allow to evaluate the correct encapsulation capacity of nitrogen, phosphorus, and potassium in microparticles with fertilization purposes are of great importance, since these controlled release systems promise to be more efficient and minimize the environmental impacts compared to conventional fertilization.

## 1. Introduction

Controlled release polymeric microstructured systems can be defined as solid colloidal particles with a maximum size of 1000 µm, which carry an active substance for subsequent slow and controlled release in the medium for which they have been developed[1]. Due to this property, these systems have some advantages, including reduction in the number of chemical substances needed in their applications, propensity to reduce the risk of contamination, ability to reduce the amount of energy spent since the number of necessary applications is reduced and to maintain the concentration of the substance for a greater period of time[2–5].

In this way, this technology allows a change in the physicochemical properties of the active principles, making it an interesting alternative for the controlled/proper release of nitrogen, phosphorus and potassium (NPK), since traditional fertilizers may lose part of their nutrients when applied to the environment, leading to unwanted environmental contamination[6–9]. Therefore, the controlled/modified release technology becomes an important alternative that minimizes the problems caused by traditional fertilizers.

There are several determining factors in the choice of the preparation method, namely: the type of polymer(s) to be used, the application site of the particles and the desired size, among others[10,11]. In view of this, the emulsification solvent diffusion method is attractive, given that it is easy to apply and it is highly reproducible and compatible with biodegradable polymers. The emulsification solvent diffusion method was first described by Fessi (1988)[12]. It consists of the interfacial polymer deposition after the displacement of a water-miscible semipolar solvent from a lipophilic solution[13,14]. This method has been extensively reported in the literature and applied to a wide range of active principles[15–17].

There are some studies in the literature that have used poly(ε-caprolactone) (PCL) for the synthesis of microparticles carrying several micro-active substances of interest, such as pharmaceuticals and herbicides, via the emulsification solvent diffusion method, among others[18–23]. Poly(ε-caprolactone) is an aliphatic biodegradable polyester, insoluble in water, that has slow degradation in aqueous medium and poses no environmental harm. As a result, it is chosen for the synthesis of carrier systems.

In addition to aliphatic polyesters, alginate polymers can be used for the synthesis of controlled release systems[24,25]. The properties of polyglycerol (PG) are like those of alginate polymers and is obtained by glycerine polymerisation, which is abundantly generated during biodiesel production. For this reason, the development of processes that fosterers the use of this residual glycerine is of great importance, because it exhibits an interesting environmental aspect. One of them[26] is using this residual glycerine via PG to synthesise controlled release systems, providing an alternative use/reuse of this large-scale produced industrial waste with no relevant applications.

In view of the characteristics, the microparticulate system synthesized with PCL and PG developed in the present study was used to encapsulate three essential nutrients for plants, nitrogen, phosphorus and potassium. These nutrients are classified as macronutrients because they are necessary at higher concentrations (mmol $kg^{-1}$ – dry matter), compared with other essential nutrients used for plants[27].

Nitrogen is essential because it promotes vigorous plant growth and is one of the responsible substances for protein development. Phosphorus promotes cell division and the formation of the cell structures of the plants. It stimulates healthy root growth, is essential for seed germination and assists in the conversion of solar energy into chemical energy for the photosynthesis process. Potassium promotes the formation of fruits and confers resistance to diseases and high temperatures. It is essential for photosynthesis and is responsible for maintaining water levels in the plants[27–29].

There are few reports in the literature[30,31] concerning the quantification of NPK in microstructured release polymeric systems. Therefore, the application and validation of analytical methods for the quantification of these chemicals in such systems is important, since these particles can provide a new direction for fertilization procedures. Consequently, the goal of the present study was to apply and validate analytical methods for determining NPK in polymeric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microparticles obtained by the emulsification solvent diffusion method, with fertilization purposes.

## 2. Experimental

### *2.1 Reagents and solutions*

The following reagents were used for the synthesis of the microparticles: boric acid (Sigma Aldrich); nitric acid (Sigma Aldrich); sulphuric acid (Synth); methyl orange (Sigma Aldrich); polyvinyl alcohol (PVA) (Sigma Aldrich); methylene blue (Sigma Aldrich); sodium carbonate (Synth); stannous chloride (Sigma Aldrich); chloroform (Sigma Aldrich); ethanol (Sigma Aldrich); phenolphthalein (Synth); glycerol (Synth); sodium hydroxide (Sigma Aldrich); ammonium molybdate (Sigma Aldrich); phosphorus, nitrogen, and potassium (999 ± 4 mg $L^{-1}$) (Sigma Aldrich); poly (ε-caprolactone) (Sigma Aldrich); polyglycerol (70wt.%) (Verti Ecotechnologies UFMG); copper sulphate (Sigma Aldrich) and methyl red (Sigma Aldrich).

All solutions were prepared using analytical-grade reagents and the final volumes were adjusted with deionized water (Milli-Q system - Millipore Corporation). The glassware was previously washed in baths containing 10%v/v nitric acid ($HNO_3$) (Synth) for 24 h. All solutions used were stored and kept at 8 °C for preservation.

### *2.2 Instrumentation*

The instruments used in this study were: magnetic stirrer (Hot Lab II Nalgon), hot plate (Hidrosan; 50 to 320 °C), macro-Kjeldahl distillation apparatus (Quimis), oven (Ethik Technology, Nova Ética - 404/D; 50 to 200 °C), atomic absorption spectrophotometer (SpectrAA 50 B - Varian) and spectrophotometer (UV-Vis 220-2000UV - Biospectro).

### *2.3 Preparation of microparticles*

The polymeric microparticles were prepared according to the emulsification solvent diffusion method described by Chagas *et al.*[30] and involves the interfacing deposition of the polymer after the displacement of a semipolar solvent, miscible in water, from a lipophilic solution. For this study, the organic phase was prepared with PCL and PG polymers. The aqueous phase was composed of PVA, deionized water and an aliquot of NPK standard solution. After the dissolution of the components of both phases, the organic phase was added to the aqueous one.

### *2.4 Kjeldahl method for quantification of nitrogen in polymeric microparticles*

The quantification of nitrogen was carried out according to the Kjeldahl method. It consisted of digesting 100 mL of the sample with 50 mL of digesting solution (134 g of potassium sulphate and 7.3 g of copper sulphate, weighted in an analytical balance, and 134 mL of sulfuric acid for 1 L of solution) in a hot plate at 320 °C. Then, 300 mL of distilled water were added along with 50 mL of sodium hydroxide (50% w $v^{-1}$)/sodium thiosulphate (2.5% m $v^{-1}$) solution to the solution resulting from the digestion. This mixture was made in a Kjeldahl flask using a measuring cup. Subsequently, the sample was submitted to distillation in a traditional Kjeldahl distiller. The product of this reaction was collected in 50 mL boric acid solution presented in an Erlenmeyer flask. This acid solution was produced with 0.0200 g of methyl red, 10 mg of methylene blue and 20 g of boric acid, weighed in analytical balance, in ethanoic acid medium. Then, the titration of the distilled solution with sulphuric acid (0.01 mol $L^{-1}$) was performed[32]. The analytical curve was constructed with serial dilutions of a standard nitrogen solution (1000 mg $L^{-1}$).

### *2.5 Stannous chloride method for the quantification of phosphorus in polymeric microparticles*

The quantification of phosphorus was made according to the stannous chloride method[32]. It was performed a 100-times dilution of the particulate suspension, in which the diluted samples were digested with 1 mL of concentrated sulphuric acid and 5 mL of concentrated nitric acid in a hot plate at 250 °C. Later,


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20 mL of distilled water and 0.05 mL of phenolphthalein were added to the filtrate solution. This solution was neutralised with sodium hydroxide solution (NaOH) (6.00 mol $L^{-1}$). Subsequently, this solution was titrated with a solution obtained by mixing concentrated sulfuric and nitric acids. Finally, 4 mL of ammonium molybdate solution (25 g of ammonium molybdate, weighted in analytical balance, and 280 mL of sulphuric acid for one liter of solution) and 0.50 mL of the stannous chloride solution (2.5 g of stannous chloride, weighted in analytical balance, for 100 mL of glycerol) were added. Then, the solution was analyzed in a UV-Vis spectrophotometer at 690 nm with a 10 mL glass cuvette. The analytical curve was constructed with serial dilutions of a standard phosphorus solution (1000 mg $L^{-1}$).

### *2.6 Development of the potassium quantification method in polymeric microparticles*

The quantification of potassium was carried out by flame atomic absorption spectrophotometry, in which the conditions were: 5 mA for the lamp current, air/acetylene flame and air support, flame stoichiometry adjusted to obtain an oxidizing environment, wavelength of 766.55 nm and slot width of 1.0 nm. For the preparation of the samples, a multivariate optimization study was conducted to adequate the ideal conditions, previously studied and reported by the research group involved in this work[32]. The most efficient digestion occurred with 5 mL of the filtrate solution and 10 mL of concentrated nitric acid at 60 °C under magnetic stirring for 90 min. The solutions resulting from the digestion were measured in a 100 mL volumetric flask and later analyzed for the quantification of potassium. The analytical curve was constructed with serial dilutions of a standard potassium solution (100 mg $L^{-1}$).

### *2.7 Methods validation*

The quantification methods were validated according to a guideline document (DOQ-CGCRE-008: 3 Revision - Feb/2010) of the National Institute of Metrology, Standardization and Industrial Quality (INMETRO)[33].

### *2.8 Specificity*

To confirm the specificity of the methods, the absence of interference caused by substances that are part of the microparticles (PCL, PG and PVA) was checked. In this way, the microparticles were prepared without the nutrients (NPK) and analyzed under the same experimental conditions of samples with the presence of nutrients.

### *2.9 Linearity, limit of quantification and limit of detection*

The linearity of the methods was determined using three analytical curves carried out in three different days, generating a total of nine curves with several concentrations diluted in water. Three analyses of each solution were performed to check the repeatability of the methods responses in each concentration. The limit of detection (LOD) and the limit of quantification (LOQ) were calculated using the slope and the standard deviation of the mean intercept in three calibration curves of each method.

### *2.10 Accuracy*

The accuracy of the methods was assessed by the standard addition of solutions with known concentrations of each nutrient to the samples of microparticle suspensions (without nutrients). The recovery was determined as the percentage difference between the average experimental concentration and the theoretical concentration at each level.

### *2.11 Precision*

The precision was determined by means of repeatability (intraday) and intermediate precision (interday). The repeatability was assessed analyzing samples of microparticles (without NPK) with standard addition of each nutrient solution on the same day and under the same experimental conditions. For the intermediate precision, the analyses were performed on three different days.


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### *2.12 Compatibility of the samples*

The matrix can have a considerable effect on the way the chemical analysis is conducted and in the quality of the results. Such effects are called matrix effects. The most common approach for the compatibility of matrix effects is the construction of a calibration curve with standard samples of known analyte concentrations, which attempts to approximate the matrix of the sample as much as possible[34].

Thus, samples of 5 mL aliquots of previously digested polymeric microparticles were transferred into 100 mL volumetric flasks. It was added N, P and K standard solutions into these flasks to obtain the analytical curves for every chemical element. The analyses were performed in triplicate for each used method. An acid solution previously prepared according to each method was used as a solution with no matrix effects.

### *2.13 Tendency/recovery*

When applied to a series of test results, tendency implies a combination of random and systematic error components. The latter cannot be admitted. Tendency can be expressed as analytical recovery defined by the Eq. 1[33].

$$\text{Recovery} = \frac{\text{observed value}}{\text{expected value}} \times 100\% \quad (1)$$

### *2.14 Determination of encapsulation efficiency*

The percentage rate of nutrients combination (NPK) [encapsulation efficiency (EE)] in the microparticles is of great importance, because it is the condition that will indicate the concentration of the active principle that the polymeric particles are able to blend for the subsequent controlled release[35,36].

The percentage of NPK blend with the microparticles was determined by specific methods for each chemical element. Samples of 100 mL microparticles suspension containing NPK were filtered in quantitative filter paper (slow filtration - blue ribbon 3552, Nalgon). Then, the EE was determined by the difference between the quantification of nutrients concentrations in the filtrate solution and their total concentration (100%) present in the microparticles suspension (Eq. 2)[35,36].

$$\text{EE (\%)} = \frac{(X_o - X_f)}{X_o} \times 100\% \quad (2)$$

where $X_o$ is the nutrient concentration quantified in the solution of microparticles and $X_f$ is the nutrient concentration quantified in the filtered solution of microparticles.

### *2.15 Morphological analysis of the particles*

The particle synthesis procedure reported in the Chagas *et al.*[30], was performed. In this way, the suspension obtained was filtered and the retained material was dried in a desiccator. After complete drying, 10 mg of the sample were placed on a carbon ribbon. The samples were taken to a vacuum metallizer for the deposition of gold (100 to 200 nm). Then, the morphology of the samples of metallized particles using a scanning electron microscope (SEM) were analyzed. Size distributions were measured and expressed as means of three determinations.

## 3. Results and discussion

### *3.1 Morphological analysis of the particles*

The SEM analysis of the particles indicated that the formulation used for the synthesis was efficient (Fig. 1). Spherical particles without aggregates were observed. The average size ranged from 5 to 60 µm and the particles were classified as microparticles. To be considered nanoparticles, the average diameter should be less than 1000 nm[30,31, 34–36], as presented in a previous work[30].


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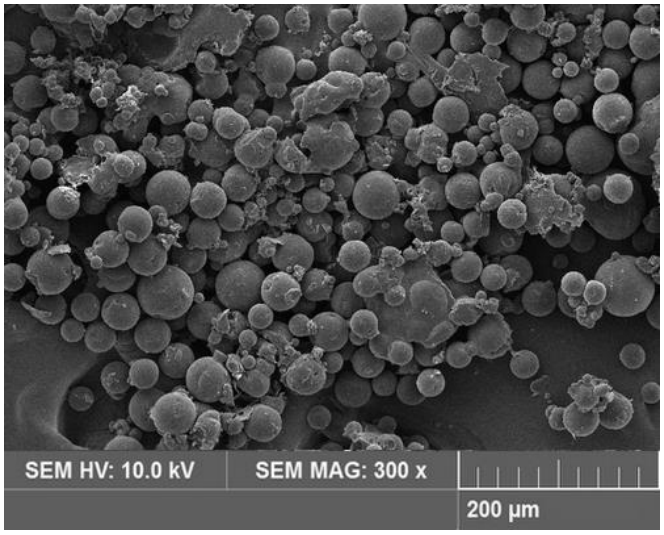


**Figure 1.** Scanning electron microscope images of the polymeric microparticles containing the nutrients NPK at 300 × magnification. SEM HV = scanning electron microscope high vacuum; MAG = magnification.

### *3.2 Validation of the proposed analytical methods*

The linearity of the analytical methods was assessed using linear regressions of nine analytical curves for each nutrient and each point on the curve was analyzed three times (intraday-interday). The correlation coefficients (r) of the mean analytical curves (n = 9) and the respective parameters (A and B) are shown in Tab. 1. The validity of the regression is observed when the slope of the curve is significantly different from zero, which is represented by values of $F_{cal}$ (calculated F) less than that of $F_{tab}$ (tabulated F). The calculated values for F of the three nutrients (NPK) are shown in Tab. 1, they are smaller than the $F_{tab}$ value, thus it is assumed that the slope of the line is not zero and the linear curve fit is accepted for both nutrients with $p < 0.0001$. In this way, it can be affirmed with 95% confidence that the model is linear and well-adjusted in the concentration range studied[37]. The correlation coefficient is a parameter that allows to estimate the quality of the obtained curve because the closer to 1, the smaller the dispersion of the experimental points. The National Health Surveillance Agency (ANVISA/Brazil) and the National Institute of Metrology, Standardization and Industrial Quality (INMETRO/Brazil) recommend a correlation coefficient greater than or equal to 0.99[33]. All linear correlation values shown in Tab. 1 for R were above 0.99, therefore, each method was considered linear[33,34]. The results indicate that the sampling conditions proposed in this study are adequate for the analysis of NPK in the investigated levels, 10.00 to 20.00 mg $L^{-1}$ for N; 0 to 2.40 mg $L^{-1}$ for P and 0 to 2.00 mg $L^{-1}$ for K[30].

**Table 1.** Parameters obtained with the linear regressions of the analytical curves for NPK nutrients.

| Nutrient | Interval | Parameters | Results | Statistic α < 0.05 |
|---|---|---|---|---|
| Nitrogen | 10.00 to 20.00 mg $L^{-1}$ | Slope | 0.3 ± 0.1 | $F_{cal}$ = 3.9253<br>$F_{tab}$ = 4.62 |
| | | Intercept | 0.2 ± 0.3 | $F_{cal}$ = 1.0692<br>$F_{tab}$ = 4.62 |
| | | R | 0.999 ± 0.001 | |
| Phosphorus | 0.00 to 2.00 mg $L^{-1}$ | Slope | 1.859 ± 0.004 | $F_{cal}$ = 1.4100<br>$F_{tab}$ = 4.62 |
| | | Intercept | 0.015 ± 0.007 | $F_{cal}$ = 1.3856<br>$F_{tab}$ = 4.62 |
| | | R | 0.9992 ± 0.0003 | |
| Potassium | 0.00 to 2.40 mg $L^{-1}$ | Slope | 0.072 ± 0.008 | $F_{cal}$ = 8.4279<br>$F_{tab}$ = 39.45 |
| | | Intercept | 0.0026 ± 0.0007 | $F_{cal}$ = 1.3074<br>$F_{tab}$ = 4.62 |
| | | R | 0.9993 ± 0.0007 | |

NPK = nitrogen, phosphorus, and potassium; R = correlation coefficient; $F_{cal}$ = calculated F; $F_{tab}$ = tabulated F.


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Repeatability, or intraday precision, was evaluated by the determination of the intraday RSD and the intermediate precision, or interday precision, was determined by the interday RSD. The RSD values are shown in Tab. 2.

**Table 2.** Values of the relative standard deviation (RSD) of NPK concentrations (C) for assessing the methods precision.

| Nutrient | C / mg $L^{-1}$ | RSD - day 1 / % | RSD - day 2 / % | Interday RSD / % |
|---|---|---|---|---|
| **N** | 5.00 | 0.72 | 0.81 | 0.72 |
| | 10.00 | 2.02 | 2.14 | 2.52 |
| | 15.00 | 2.95 | 4.30 | 1.73 |
| **P** | 0.45 | 2.18 | 3.45 | 2.67 |
| | 0.75 | 0.78 | 1.32 | 3.52 |
| | 1.15 | 1.77 | 2.28 | 1.77 |
| **K** | 0.04 | 1.50 | 1.50 | 1.44 |
| | 0.60 | 4.03 | 1.61 | 1.53 |
| | 1.20 | 1.74 | 3.85 | 4.94 |

C = concentration; RSD = relative standard deviation.

The intra and interday RSD values determined in Tab. 2 were all below the limit established by ANVISA and the Institute of Human Sciences (IHC), which is a maximum of 5%[33,34]. Therefore, the methods could be considered accurate. The accuracy was determined by experimentally determined concentration values, compared with the theoretical concentrations, as shown in Tab. 3.

**Table 3.** Nitrogen, phosphorus, and potassium concentration values determined for assessing the methods accuracy.

| Nutrient | Theoretical concentration / mg $L^{-1}$ | Empirical concentrations / mg $L^{-1}$ | Recovery / % |
|---|---|---|---|
| **N** | 5.00 | 5.39 | 107.80% |
| | 5.00 | 5.37 | 107.40% |
| | 5.00 | 5.45 | 109.00% |
| | 10.00 | 10.48 | 104.80% |
| | 10.00 | 10.34 | 103.40% |
| | 10.00 | 10.21 | 102.10% |
| | 15.00 | 15.20 | 101.30% |
| | 15.00 | 15.00 | 100.00% |
| | 15.00 | 14.80 | 98.60% |
| **P** | 0.25 | 0.24 | 96.00% |
| | 0.25 | 0.26 | 108.00% |
| | 0.25 | 0.24 | 96.00% |
| | 0.55 | 0.53 | 96.00% |
| | 0.55 | 0.53 | 96.00% |
| | 0.55 | 0.54 | 98.18% |
| | 1.15 | 1.20 | 104.34% |
| | 1.15 | 1.19 | 103.48% |
| | 1.15 | 1.14 | 99.14% |
| **K** | 0.06 | 0.06 | 101.67% |
| | 0.06 | 0.05 | 98.33% |
| | 0.06 | 0.05 | 98.33% |
| | 0.30 | 0.32 | 106.60% |
| | 0.30 | 0.32 | 108.00% |
| | 0.30 | 0.31 | 103.30% |
| | 1.20 | 1.16 | 97.25% |
| | 1.20 | 1.18 | 98.33% |
| | 1.20 | 1.14 | 95.50% |

N = nitrogen; P = phosphorus; K = potassium.


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Accuracy is the relationship between experimentally determined mean concentrations and the corresponding theoretical ones. The recovery percentage varied from 95.50 to 108%. In this way, all results achieved the established acceptance criteria for concentrations (from 95 to 110%) and the methods were considered accurate[33,34]. The LOD and LOQ using the data obtained with the linear regressions were also determined (Tab. 4).

**Table 4.** Limit of detection (LOD) and limit of quantification (LOQ) values for the developed methods to analyse NPK in polymeric microparticles.

| Nutrient | LOD / mg $L^{-1}$ | LOQ / mg $L^{-1}$ |
|---|---|---|
| N | 5.04 | 5.32 |
| P | 0.046 | 0.110 |
| K | 0.042 | 0.051 |

The compatibility of the samples was assessed through the experimentally determined concentration values in solutions prepared with solvents, compared with solutions prepared without NPK (Figs. 2, 3 and 4).

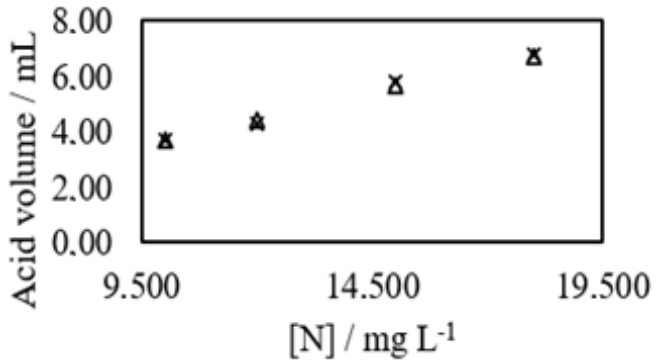


**Figure 2.** Curves for the assessment of compatibility of samples in the analyses of N from polymeric microparticles using the Kjeldahl method (n = 3).
Triangle = curve prepared with solutions in solvent. X = curve prepared with polymeric microparticles.

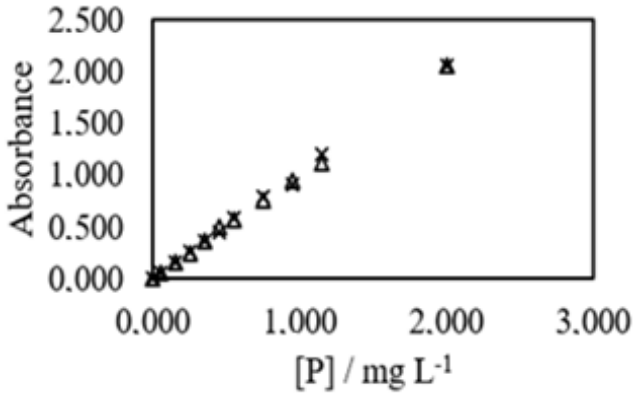


**Figure 3.** Curves for the assessment of compatibility of samples in the analyses of P from polymeric microparticles using the stannous chloride method (n = 3).
Triangle = curve prepared with solutions in solvent. X = curve prepared with polymeric microparticles.

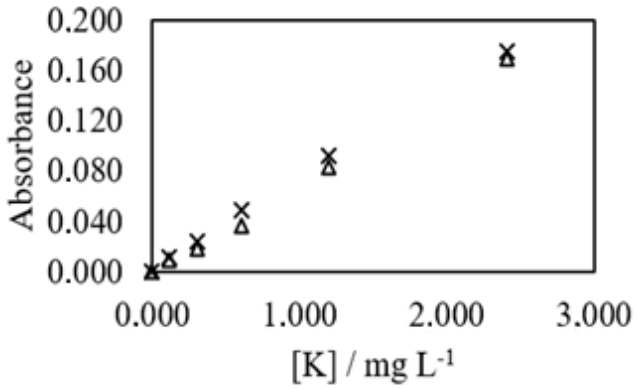


**Figure 4.** Curves for the assessment of compatibility of samples in the analyses of K from polymeric microparticles using flame atomic absorption spectrophotometry (n = 3).
Triangle = curve prepared with solutions in solvent. X = curve prepared with polymeric microparticles.

The correlation coefficients of the analytical curves of solutions in solvent medium and microparticle medium (n = 3) with their respective parameters (A and B) of the regression equations presented in Figs. 2, 3 and 4 are shown in Tab. 5.


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**Table 5.** Parameters obtained with the linear regressions of the analytical curves of solutions in solvent medium and microparticle medium for the NPK nutrients.

| Nutrient | Solutions in solvent medium | | | Solutions in microparticle medium | | |
|---|---|---|---|---|---|---|
| | A | B | R | A | B | R |
| N | 0.3906 | 0.2468 | 0.9987 | 0.4044 | 0.4262 | 0.9972 |
| P | 1.0261 | 0.0040 | 0.9987 | 1.0117 | 0.0025 | 0.9984 |
| K | 0.0586 | 0.0028 | 0.9990 | 0.0577 | 0.0018 | 0.9993 |

A = slope; B = intercept; R = correlation coefficient.

The results obtained, showed in Tab. 5, indicate that the correlation and the angular and linear coefficients of the curves had no significant difference. Therefore, the methods used did not require compatibility of samples and the analytical curves prepared in solvents could be used.

All validation parameters assessed for the analytical methods proposed were considered satisfactory since they met the specifications established by ANVISA and INMETRO[33,37]. Therefore, the methods could be considered s pecific, linear, precise and accurate. As a result, they are applicable in analysis for determining NPK in polymeric microparticles.

### *3.3 Application of the proposed methods to determine the encapsulation efficiency and NPK content*

The microparticles obtained were analyzed using each specific method previously validated in this work to determine the efficiency of NPK encapsulation. The encapsulation values were then determined by the difference between the total concentration (100%) of the nutrients present in the microparticle suspension and the quantified ones in the filtered solution of microparticles[30]. The results are shown in Tab. 6.

The values of EE percentage shown in Tab. 6 were satisfactory, since there are few studies in the literature assessing the EE percentage for the active substances proposed in the present study with the use of polyglycerol. In addition, these values were within the averages shown in the literature for other active principles[18–23,38–41]. The differences in the values for the encapsulation showed in Tab. 6 are due to the results related to the multivariate experimental designs employed, in which each assay promotes different levels of the investigated parameters and, as a result, a different response can be generated. This study was previously discussed and published by this group[30].

**Table 6.** Results of encapsulation efficiency (EE) through the application of the developed analytical methods for the quantification of NPK in polymeric microparticles.

| Sample | EE per nutrient / % | | |
|---|---|---|---|
| | Nitrogen | Phosphorus | Potassium |
| **01** | 96.27 | 96.58 | 59.62 |
| **02** | 83.80 | 77.80 | 48.60 |
| **03** | 93.68 | 77.60 | 27.80 |
| **04** | 87.64 | 99.20 | 43.00 |
| **05** | 70.08 | 80.60 | 29.40 |
| **06** | 47.58 | 91.60 | 45.20 |
| **07** | 61.85 | 81.00 | 34.60 |
| **08** | 78.31 | 95.60 | 33.00 |
| **09** | 78.31 | 96.20 | 36.20 |

The highest values of the nitrogen and phosphorus encapsulations in polymeric microparticles were because these nutrients feature high aqueous solubility, which promotes high interaction with PG[4]. The lowest rate of potassium encapsulation, in comparison with the other nutrients, can be explained by the interaction competition between N and P. The developed and validated analytical methods are applicable to samples of polymeric microparticles.

Although the analytical methods applied here are well established in the literature, from the best of the author's knowledge, their application to the types of samples described in this research were not found, except to those previously published by our research group[30].

## 4. Conclusions

The proposed analytical methods for detection and quantification of NPK in microparticles, i.e., Kjeldahl,


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stannous chloride and flame atomic absorption spectrophotometry, respectively, proved to be specific, linear, accurate and precise in the concentration ranges assessed. They are suitable for determining encapsulation efficiency and NPK contents in poly(ε-caprolactone) and polyglycerol microparticles.

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