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Coordination polymer adsorbent for matrix solid-phase dispersion extraction of pesticides during analysis of dehydrated *Hyptis pectinata* medicinal plant by GC/MS

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ABSTRACT

The coordination polymer $[Zn(BDC)(H_2O)_2]_n$ was tested for extraction of pyrimethanil, ametryn, dichlofluanid, tetraconazole, flumetralin, kresoxim-methyl and tebuconazole from the medicinal plant *Hyptis pectinata*, with analysis using gas chromatography–mass spectrometry in selected ion monitoring mode (GC/MS, SIM). Experiments carried out at different fortification levels (0.1, 0.5 and 1.0 $\mu g\,g^{-1}$) resulted in recoveries in the range 73–97%, and RSD values were between 5 and 12% for the $[Zn(BDC)(H_2O)_2]_n$ sorbent. Detection and quantification limits ranged from 0.02 to 0.07 $\mu g\,g^{-1}$ and from 0.05 to 0.1 $\mu g\,g^{-1}$, respectively, for the different pesticides studied. The method developed was linear over the range tested (0.04–14.0 $\mu g\,g^{-1}$), with correlation coefficients ranging from 0.9987 to 0.9998. Comparison between $[Zn(BDC)(H_2O)_2]_n$ and the commercial phase C_{18}-bonded silica showed good performance of the $[Zn(BDC)(H_2O)_2]_n$ polymeric sorbent for the pesticides tested.

1. Introduction

Coordination polymers are an extensive class of crystalline materials with high stability, organic functionality and well-defined architectures, which form an important interface between materials science and synthetic chemistry [1–4]. These substances offer promising potential applications in gas sorption, separation and storage [5,6], catalysis [7,8], drug delivery [9,10] and as a stationary phase for chromatography [11,12]. Coordination polymers containing zinc and terephthalic acid residues as linkers have been extensively studied, with the most relevant work being that by Yaghi and co-workers [13–15]. However, the exploitation of coordination polymers as sorbents for solid-phase extraction has been rarely reported [12]. Research on new materials for the extraction, purification and separation of compounds in a wide polarity range has also been stimulated by the growing interest in environmental preservation and human health protection [16,17].

Medicinal plants play an important role from both commercial and healthy-lifestyle perspectives. Towards the end of the twentieth century, the World Health Organization (WHO) estimated that an impressive 80% of the world's population probably rely mainly on natural medicines, with plant-originated medicines as the main component of this trend (in developed countries) or tradition (in developing countries). The WHO has been concerned with the need for quality assurance of herbal products, including testing for inadvertent contamination. Sources of contamination of unprocessed medicinal plants are diverse, and include adulteration with toxic botanicals, toxic metals, microorganisms and microbial toxins, radioactivity, fumigation agents and pesticides [18]. However, this work focuses on contamination of medicinal plants with pesticides. The European Pharmacopoeia has proposed methods for analysis of pesticide residues in medicinal plants, establishing maximum residue limits (MRLs) for organochlorine, organophosphorus and pyrethroid pesticides [19]. The species *Hyptis pectinata* (L.) Poit, belonging to the Lamiaceae family and known as "sambacaitá" or "canudinho", is used as a medicinal tea (infusion or decoction) for treating skin diseases, gastric disorders, nasopharyngitis, nasal congestion, fever and other infections caused by bacteria and fungi [20].

Various methods using solid-phase microextraction (SPME) [21], solid-phase extraction (SPE) [22,23], supercritical fluid extraction (SFE) [19] and matrix-solid-phase dispersion (MSPD) [24] have been described for the determination of organochlorine, organophosphorus and pyrethroid pesticides. However, no published papers have reported on the simultaneous analysis of chemical classes such as anilinopyrimidine, triazine, sulfonamide,

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triazine, dinitroaniline, strobilurin and triazole in *H. pectinata*. Nonetheless, pyrimethanil, ametryn, dichlofluanid, tetraconazole, flumetralin, kresoxim-methyl and tebuconazole are among the pesticides most commonly used for pest control in a variety of different cultivations near to medicinal herb plantations in the State of Sergipe (Brazil), as well as elsewhere.

The matrix solid-phase dispersion technique consists of the use of a sorbent or dispersing agent, acting as an abrasive in order to produce a modified "opening" of the solid matrix, facilitating the extraction process when using a suitable solvent for eluting the analytes [25]. Pesticide recovery using the MSPD procedure depends on the solubility of the pesticides in the eluting solvent, as well as on the interactions between the matrix components and the sorbent or eluent [26].

The aim of this study was to evaluate the performance of $[Zn(BDC)(H_2O)_2]_n$ as a new adsorbent material for matrix solid-phase dispersion in the determination of pesticides of seven chemical classes, namely anilinopyrimidine (pyrimethanil), triazine (ametryn), sulfonamide (dichlofluanid), triazine (tetraconazole), dinitroaniline (flumetralin), strobilurin (kresosim-methyl) and triazole (tebuconazole), in the medicinal plant *H. pectinata*, using gas chromatography–mass spectrometry.

2. Experimental

2.1. Standards, reagents and supplies

Certified standards of pyrimethanil, ametryn, dichlofluanid tetraconazole, flumetralin, kresoxim-methyl and tebuconazole standards were purchased from AccuStandard (New Haven, CT, USA) at purities greater than 95%. Dichloromethane was pesticide grade (Tedia, Fairfield, OH, USA). Analytical grade anhydrous sodium sulfate was supplied from Mallinckrodt Baker (Paris, KY, USA). Sodium terephthalate (Na_2BDC, 96%) and $Zn(NO_3)_2{\cdot}6H_2O$ (98%) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Chemicals were used as received and without further purification.

2.2. Pesticide standard solutions

Stock standard solutions of the pesticides were prepared by precisely weighing out and then dissolving the compounds in dichloromethane to give concentrations of 200 $\mu g\,g^{-1}$. These standard solutions were stored at −18 °C, and were stable for a period of at least 2 months. Working standard solutions were prepared by diluting the stock solutions in dichloromethane as required. Matrix-matched standards were prepared at the same concentrations as those of calibration solutions by adding appropriate amounts of standards to the control matrix extract.

2.3. Synthesis of $[Zn(BDC)(H_2O)_2]_n$

A mixture of Na_2BDC (0.50 mmol, 0.105 g), $Zn(NO_3)_2{\cdot}6H_2O$ (1.00 mmol, 0.297 g) and H_2O (*ca.* 12 mL) was placed in a 30 mL Teflon-lined Parr Instruments stainless steel autoclave, which was transferred to an oven (Venticell MMM, Medcenter Einrichtungen GmbH), preheated to 120 °C, for 72 h. The final compound was obtained in high yield (*ca.* 93%, based on the ligand), after being washed with water and acetone and then air-dried.

2.4. Solid-phase characterization

Elemental analysis was performed using a CNHS analyzer (CE Instruments, model EA1110). Infrared spectra were recorded with a Bruker IFS 66 spectrometer, in the range 4000–400 cm^{-1}, using the conventional KBr technique. Thermogravimetric data (TGA) were obtained in the 25–800 °C temperature range for *ca.* 3.0 mg of each sample, using a thermobalance (Shimadzu model TGA 50) fitted with a platinum crucible, under a dynamic nitrogen atmosphere (50 mL min^{-1}) and with a heating rate of 10 °C min^{-1}. Scanning electron microscopy (SEM) images were obtained using an SU-70 microscope operated at 15 kV. X-ray powder diffraction analyses were performed at room temperature, using a Rigaku RINT2000 diffractometer with a rotating copper anode ($\lambda k\alpha_1$ = 1.5404 Å, $\lambda k\alpha_2$ = 1.5444 Å, $I\alpha_2/I\alpha_1$ = 0.5). Intensity data were collected in step scanning mode, in the range from 5 to 50° (2θ), with a step size of 0.01°, Soller slit with 2.5° of divergence, 0.5° scattering slit and 0.3 mm receiving slit. Rietveld structural refinements [27] were performed using the crystal structure model described by [28], using TOPAS-Academic software [29]. The orientation was corrected according to the spherical harmonics model described by Jarvinen [30].

2.5. Sample preparation

The dehydrated sambacaitá samples were purchased in the municipal market of Aracaju, Sergipe State (Brazil). They were brought to the laboratory and stored in plastic bags at ambient temperature until processing. In the laboratory, samples were ground using a food processor and stored in screw cap vials. Recovery experiments were performed using 0.5 g of sambacaitá sample, spiked with 500 μL of working standard solution, resulting in concentrations of 0.05, 0.1, 0.5, and 1.0 $\mu g\,g^{-1}$. The spiked samples were allowed to rest for 30 min to help solvent evaporation and interaction between analytes and sample matrix (five replicates were analyzed for each fortification level). The extraction procedure is described below.

2.6. Extraction procedure

A spiked aliquot of sambacaitá (0.5 g) was placed into a glass mortar (*ca.* 50 mL), and 0.5 g of $[Zn(BDC)(H_2O)_2]_n$ was added. The sample was then gently blended into the sorbent material with a glass pestle, until a homogeneous mixture was obtained (*ca.* 3 min). The homogenized mixture was introduced into a 100 mm × 20 mm i.d. polypropylene column, filled with 0.1 g of glass wool at the base, and 1.0 g of anhydrous Na_2SO_4. The elution was performed under vacuum with 20 mL of dichloromethane. The eluent was collected into a graduated conical tube and concentrated using a rotary vacuum evaporator (35 °C), and finally purged with a gentle stream of nitrogen to a volume of 1 mL. An aliquot of 1 μL was analyzed by GC/MS.

2.7. GC/MS system and operating conditions

A Shimadzu (Kyoto, Japan) system consisting of a QP-2010Plus mass spectrometer coupled to a GC 2010 gas chromatograph, with a Shimadzu AOC 20i autosampler and a split/splitless injector, was used for the identification and quantification of the pesticides. A fused-silica RTx-5MS column (5% phenyl–95% polydimethylsiloxane, 30 m × 0.25 mm i.d., 0.25 μm film thickness), supplied by Restek (Bellefonte, PA, USA), was employed, with helium (purity 99.995%) as carrier gas at a flow rate of 1.2 mL min^{-1}. The GC oven temperature was programmed from 60 °C (1.0 min) to 290 °C (3 min), at 10 °C min^{-1}. The solvent delay was 5 min. The injector port was maintained at 250 °C, and 1 μL sample volumes were injected in splitless mode (50 s). The data were acquired and processed on a personal computer, using Shimadzu GC Solution software. The total analysis time was 27 min, and the equilibration time was 2 min. The eluent from the GC column was transferred, via an interface line heated to 280 °C, into the 70 eV electron ionization source, also maintained at 280 °C. The analysis was performed in the selected ion monitoring (SIM) mode. For the first acquisi-

tion window (5.0–17.5 min), the ions monitored were *m/z* 183, **198** and 199 (pyrimethanil, 16.9 min). For the second acquisition window (17.5–19.5 min) *m/z* 185, **212** and 227 (ametryn, 18.1 min), *m/z* 123, 167 and **224** (dichlofluanid, 18.6 min), *m/z* 171, **336** and 338 (tetraconazole, 18.9 min) were monitored. For the third acquisition window (19.5–27.0 min), *m/z* 145, **157** and 404 (flumetralin, 20.3 min), *m/z* 131, **206** and 282 (kresoxim-methyl, 20.9 min) and *m/z* 125, 250 and **252** (tebuconazole, 22.8 min) were monitored. Values of *m/z* in bold type correspond to the quantification ion for each analyte.

3. Results and discussion

3.1. Characterization of $[Zn(BDC)(H_2O)_2]_n$

The identification of $[Zn(BDC)(H_2O)_2]_n$ was reported in 1999 [28]. The metal-organic framework consists of Zn^{2+} centers connected by oxygen atoms to two BDC residues, forming a 1D linear structure, and the coordination sphere of the metal cation is completed by two water molecules, forming a polyhedron described by a distorted tetrahedron. The supramolecular structure of the crystal is formed by connecting the 1D polymer chain by π–π stacking (interlayer distance of 5.003 Å) and a series of hydrogen bonds (Fig. 1). Its structure [28,31], intra-molecular interactions (that have been observed by luminescence [32]), and interesting π–π interactions suggest that the crystalline $[Zn(BDC)(H_2O)_2]_n$ material could be a useful solid phase adsorbent for aromatic groups. Therefore, in this work the synthetic procedure reported in the literature [28,31,32] was modified with the objective of increasing overall crystallinity, with rearrangement into parallel-stacked structures for greater intra-molecular interaction. The hydrothermal reaction using a 1:2 ligand–metal ratio supplied excellent material, moreover the compounds could be isolated as large and very well-formed single crystals (crystal size in the *ca.* 50–100 μm range), as revealed by the SEM images.

Elemental analyses were in good agreement with the calculated values. For $C_8H_8O_6Zn$ calculated values (%) are 36.17 (C) and 3.04 (H), while measured values were 36.01 (C) and 3.12 (H). Signals observed in the infrared spectrum contain peaks characteristic of the compound (selected FT-IR data (cm^{-1}): 3322 (w), 3243 (s), 1650 (w), 1577 (s), 1504 (s) 1405 (s), 1367 (s), 1307 (w), 1014 (w), 854 (s), 748 (s), 570 (w), and 511 (w)). The thermogravimetric analysis showed three distinct weight loss events, which could be interpreted as: (i) release of the coordinated water molecules in two consecutive stages, with the first step releasing, on average, one molecule between 140 and 178 °C (*ca.* 6.8%), and the second step releasing the other remaining molecule linked to zinc metal between 179 and 206 °C (*ca.* 6.8%); (ii) degradation of the organic ligand between 207 and 600 °C (*ca.* 55.8%), leaving only the metal. These characterizations are in good general agreement with results obtained after Rietveld refinement (Fig. 2). At the end of the refinement the reliability factors [33] R_{wp}, R_{Bragg} and χ^2 were 16.75%, 5.24% and 3.658, respectively.

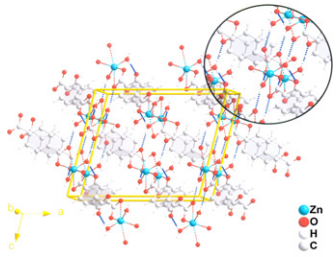

Fig. 1. Supramolecular structure showing the off-set π–π stacking between adjacent 1D chains (gray polyhedron) and the hydrogen bond (blue dashed line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

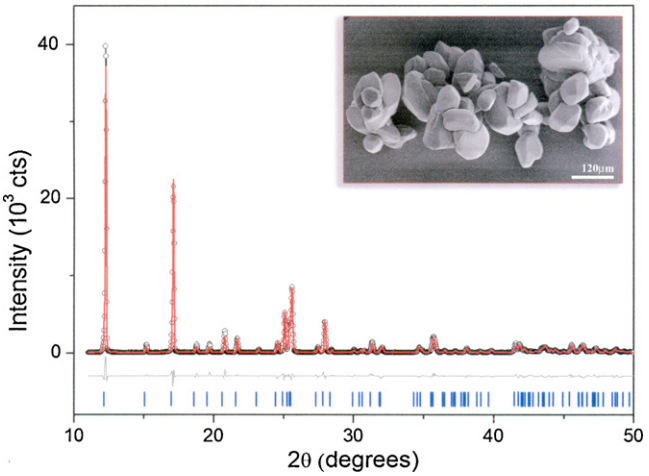

Fig. 2. SEM image of $[Zn(BDC)(H_2O)_2]_n$ and Rietveld refinement of $[Zn(BDC)(H_2O)_2]_n$: measured pattern (black circles), calculated pattern (red solid line) and difference profile (gray solid line). Blue tick marks (|) at the bottom of the pattern indicate peak positions allowed by the unit-cell parameters and space group. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

3.2. Chromatographic conditions

The retention times of the pesticides were assessed using individual standard solutions in dichloromethane, at concentrations of 10 μg g^{-1}. The GC/MS instrument was operated in full scan mode (SCAN), varying the temperature of the oven and the carrier gas flow. The most representative ions (most intense ions) were selected for quantification of the pesticides in the sambacaitá samples. It was found that there was a change in the signal intensity during the analysis, due to the matrix components. This effect was assessed by comparing the values of instrumental response (chromatographic peak area) for the pesticide solutions, with solutions prepared in the sample extract (control), at the same concentrations. For all pesticides, the peak area values were found to be higher for the sample extract. Chromatograms obtained for a standard mixture solution in dichloromethane, at 0.5 μg g^{-1}, and for a standard mixture solution in a blank sambacaitá sample after MSPD at the same concentration level, are illustrated in Fig. 3, together with a chromatogram of the sambacaitá control sample, demonstrating the selectivity of the MSPD method.

3.3. MSPD extraction procedure

The performance of the $[Zn(BDC)(H_2O)_2]_n$ polymer was compared with that of C_{18}-bonded silica, which was previously used as extracting phase during the multiclass analysis of selected pesticides in the medicinal plant *H. pectinata*, in our earlier validated MSPD procedure [34]. The maximum residue levels (MRLs) of a target compound must always be taken into account when performing recovery studies. Since there are no specific regulations or parameters for herbal drugs in Brazil, this study was based on the work of Zuin and collaborators, studying *passiflora* spp., whose MRLs established by the European Pharmacopoeia were 0.05 μg g^{-1} for dieldrin, 0.6 μg g^{-1} for lindane, 1.0 μg g^{-1} for malathion and 1.8 μg g^{-1} for tetradifon [19]. The concentration levels evaluated in this study were 0.1, 0.5 and 1.0 μg g^{-1}, consistent with the concentrations measured by Zuin et al. [19]. Average recoveries ranged from 83 to 127%, with relative standard deviations (RSD) of 5–15%, using C_{18}-bonded silica as sorbent, and from

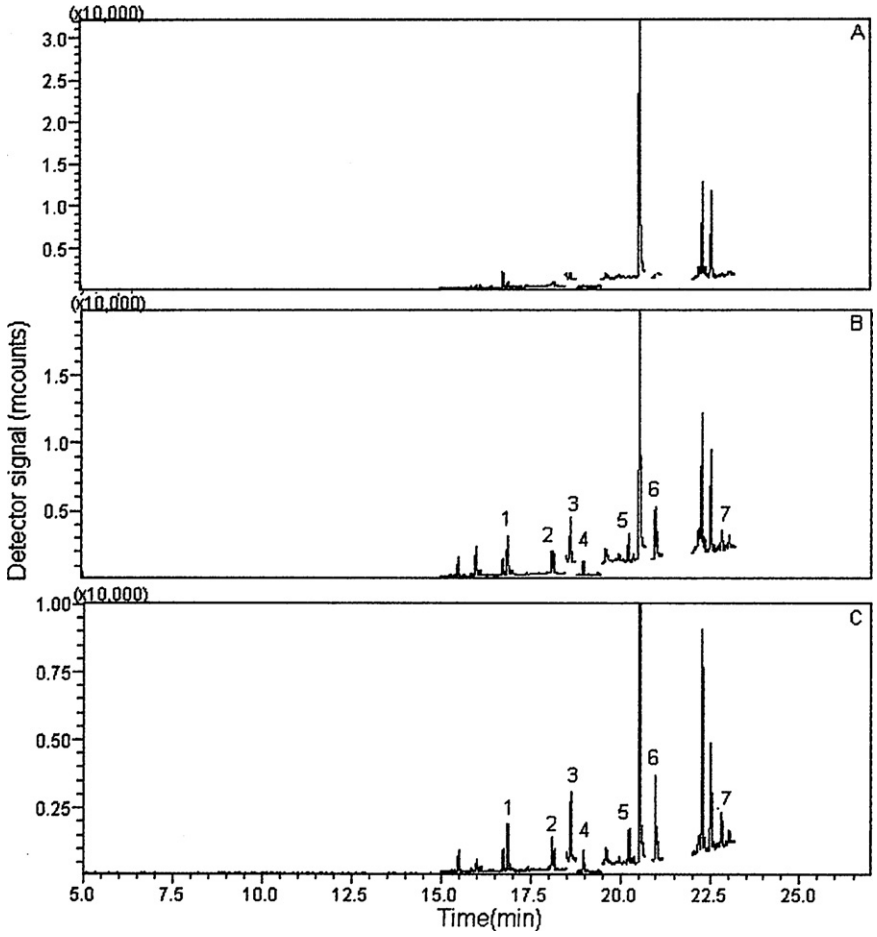

Fig. 3. GC/MS (SIM mode) chromatograms of (A) sambacaitá control sample; (B) standard mixture solution at a concentration level of 0.5 μg g^{-1} using 0.5 g of sambacaitá + 0.5 g of C_{18}-bonded silica and dichloromethane (20 mL); (C) typical sambacaitá extract fortified at a concentration level of 1.0 μg g^{-1}. The numbered peaks are as follows: 1-pyrimethanil; 2-ametryn; 3-dichlofluanid; 4-tetraconazole; 5-flumetralin; 6-kresoxim-methyl; 7-tebuconazole. See Section 2 for details on the GC/MS system and operating conditions.

Table 1
Percentage recoveries and relative standard deviations for the pesticides studied obtained using the MSPD procedure applied to the fortified sambacaitá medicinal plant.

Pesticide	Fortification level (μg g^{-1})	Mean recovery (%)[a]	
		C_{18}-bonded silica (RSD %)	$[Zn(BDC)(H_2O)_2]_n$ (RSD %)
Pyrimethanil	0.1	83 (9)	89 (8)
	0.5	108 (7)	95 (7)
	1.0	92 (8)	83 (6)
Ametryn	0.1	90 (15)	89 (10)
	0.5	104 (9)	85 (6)
	1.0	91 (8)	95 (8)
Dichlofluanid	0.1	127 (15)	97 (7)
	0.5	105 (11)	82 (12)
	1.0	99 (12)	90 (7)
Tetraconazole	0.1	88 (9)	85 (8)
	0.5	105 (11)	88 (9)
	1.0	99 (11)	81 (10)
Flumetralin	0.1	110 (6)	80 (9)
	0.5	113 (6)	92 (6)
	1.0	101 (5)	74 (8)
Kresoxim-methyl	0.1	97 (14)	92 (10)
	0.5	99 (10)	89 (12)
	1.0	90 (4)	94 (9)
Tebuconazole	0.1	96 (4)	85 (5)
	0.5	85 (8)	79 (6)
	1.0	88 (8)	73 (6)

[a] $n = 5$.

Table 2
Calibration data, limits of detection and limits of quantification for the pesticides analyzed by GC/MS.

Pesticide	Equation	r	Concentration range ($\mu g\,g^{-1}$)	LOD ($\mu g\,g^{-1}$)	LOQ ($\mu g\,g^{-1}$)
Pyrimethanil	$y = 31725.6x + 1320.89$	0.9992	0.04–14.0	0.02	0.05
Ametryn	$y = 8934.9x + 803.29$	0.9989	0.04–14.0	0.05	0.1
Dichlofluanid	$y = 24948.2x – 739.83$	0.9998	0.04–14.0	0.02	0.05
Tetraconazole	$y = 10605.6x + 859.12$	0.9987	0.04–14.0	0.05	0.1
Flumetralin	$y = 12144.7x – 401.82$	0.9998	0.04–14.0	0.07	0.1
Kresoxim-methyl	$y = 23917.4x + 1472.36$	0.9992	0.04–14.0	0.07	0.1
Tebuconazole	$y = 11574.3x + 830.35$	0.9990	0.04–14.0	0.07	0.1

73 to 97%, with RSD values of 5–12%, using $[Zn(BDC)(H_2O)_2]_n$, in recovery experiments carried out using five replicates. The values obtained were generally satisfactory, considering the recovery range normally considered acceptable (70–130%). Comparison of $[Zn(BDC)(H_2O)_2]_n$ with the commercially available C_{18}-bonded silica showed that $[Zn(BDC)(H_2O)_2]_n$ was a similar extracting phase for the pesticides investigated. Table 1 presents recoveries of the seven pesticides from sambacaitá samples. These values indicate that the method is accurate and precise for the quantification of pesticide residues in sambacaitá.

Robustness may be defined as the measure of the ability of an analytical method to remain unaffected by small but deliberate variations in method parameters, and provides an indication of its reliability during normal usage. Robustness testing is a process of systematically varying parameters and measuring the effects, either on the system or on the analytical response [35]. There was no important interference of matrix peaks in detection of the pesticides, in any of the herb samples tested. Around 32 recovery tests using different herb *H. pectinata* samples were undertaken using the method developed and the seven pesticides. The different origins of the samples did not influence the instrumental response, and routine clean-up of the insert and/or ion source box was sufficient to maintain system performance.

The linearity of a method is a measure of the range within which detector response is directly proportional to the concentration of analyte in standard solutions or samples. The linearity for all compounds was determined using blank samples fortified at concentration levels ranging from 0.04 to 14.0 $\mu g\,g^{-1}$. The slope and intercept values, together with their standard deviations, were determined using regression analyses. Linear regression coefficients for the different pesticides ranged from 0.9987 to 0.9998. The limits of detection (LOD) were calculated considering the standard deviation of the analytical noise (a value of seven times the standard deviation of the blank) and the slope of the regression line, and ranged from 0.02 to 0.07 $\mu g\,g^{-1}$. The limits of quantification (LOQ) were determined as the lowest concentration giving a response of 10 times the average of the baseline noise, calculated using seven unfortified samples. The LOQ values for these compounds ranged from 0.05 to 0.10 $\mu g\,g^{-1}$ [36]. The repeatability of the method was assessed using six successive analyses of 10 $\mu g\,g^{-1}$ of pesticide standard solution, and resultant relative standard deviations were in the range 2.4–3.8% (Table 2).

Finally, the focus of our work has been to explore the scientific and technological feasibility of application of coordination polymer material. Economic aspects were not a primary concern, but are nonetheless important. In this regard, the time required for preparation of 0.5 g of the material was 18 h, at a cost of around US $2.00.

3.4. Method application

The method developed was used to analyze samples of sambacaitá purchased in the municipal market of Aracaju, Sergipe, Brazil. No pesticides were detected in any of the samples analyzed.

4. Conclusions

The coordination polymer $[Zn(BDC)(H_2O)_2]_n$ was developed, characterized and tested for matrix solid-phase dispersion extraction applied to the multiclass analysis of pesticides in the medicinal herb *H. pectinata*. Results showed that $[Zn(BDC)(H_2O)_2]_n$ can be successfully used in analysis of pyrimethanil, ametryn, dichlofluanid, tetraconazole, flumetralin, kresoxim-methyl and tebuconazole in medicinal herbs. The new solid phase could be used in screening protocols employed by official regulatory laboratories to identify pesticides in *H. pectinata* and other medicinal herbs.

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