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Flow injection determination of carboxylate, phosphate, and sulfhydryl compounds using metal exchange complexation

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ABSTRACT

The determination of carboxylate, phosphorous, and sulfhydryl compounds has been studied using flow injection by measuring the decrease in absorbance of the Fe(III)–salicylate complex due to preferential ligand interaction with ferric ion. Targeted compounds include polycarboxylates such as sodium citrate, sodium oxalate, and EDTA, anionic phosphorous compounds such as sodium monofluoroorthophosphate, sodium trimetaphosphate, and sodium hexametaphosphate, and sulfhydryl compounds such as cysteine, glutathione, and captopril. Initial flow injection optimization has focused on citrate based on its ability to replace salicylate ion in the Fe(III)–salicylate complex causing a decrease in absorbance at 525 nm proportional to the citrate concentration. Two flow injection analysis methods are developed. In the first method, offline reaction flow injection, sodium citrate dissolved in 100 μmol L^{-1} Fe–salicylate is injected in a carrier solution of 100 μmol L^{-1} Fe–salicylate. The decrease in peak area is linear over a range of 1.36–109 μmol L^{-1} using a flow rate of 1 mL min^{-1} and an injection volume of 100 μL. The effect of pH on the Fe–salicylate complex absorbance is studied from 1 to 3.5; pH 3 shows both a high and stable complex absorbance in the visible range which provided important potential selectivity over UV detection. The limit of detection is found to be less than 57 nmol L^{-1} depending on the Fe(III)–salicylate concentration used. The second method is reverse flow injection using the sample as a flowing stream in which 3 mmol L^{-1} Fe(III)–salicylate is injected and the decrease in the response with increased sample concentration was monitored. The commercially available pharmaceutical product (Citroma)® is used to assess the accuracy and precision of the two proposed methods as compared to a reference method.

1. Introduction

Polycarboxylates such as sodium oxalate, sodium citrate, and EDTA are found in several types of detergents [1–3], food products [4] and/or pharmaceuticals both as active and inactive ingredients [5–8]. Polyphosphates such as sodium trimetaphosphate, and sodium hexametaphosphate are often used as metal sequestering agents to ensure water quality in energy applications [9]. Sodium monofluorophosphate is best known as an ingredient in marketed toothpastes [10]. Glyphosate is a widely used broad spectrum herbicide which works by inhibiting the synthesis of the aromatic amino acids [11]. Aliphatic carboxylate, phosphorous and sulfhydryl containing compounds are difficult to detect due to the lack of a good chromophore, that part of the molecule responsible for absorbance of light in the UV/vis wavelength region [12]. By chemical derivatization, a chromophoric group can be introduced into the analyte to enable the use of UV/vis detection.

Pre-derivatization reaction ester chemistry is well known for carboxylates but the same chemistry cannot be easily applied to phosphorylated compounds [13]. Total poly-phosphate or -phosphonate content in a sample can be determined by first decomposition to ortho-phosphate for colorimetric determination using molybdate [14]. Detection of phoshonates such as alendronate, used to treat bone diseases, through direct complexation with ferric ion has been reported [15]. However, detection is at 250 nm where many aromatic hydrocarbon species will interfere. Specificity of phosphorus compound detection in the visible wavelength region is possible through breakup of the Fe(III)–salicylate complex. This complex formation reaction was used in the indirect detection of phytic acid in grains using Fe(III)–salicylate through a custom multi-pumping flow system [16].

Flow injection analysis is an analytical method that enables injecting a sample into a flowing carrier solvent. It was first introduced by Ruzicka and Hansen in 1975 [17]. The main advantages of this method include, beside the availability of the instrument, the high sampling rate, increased precision, low cost and simplicity. The normal technique is often referred to as flow injection (FI) or normal flow injection (nFI) to contrast it from reverse flow injection (rFI). Johnson and Petty [18] in 1982 introduced rFI through

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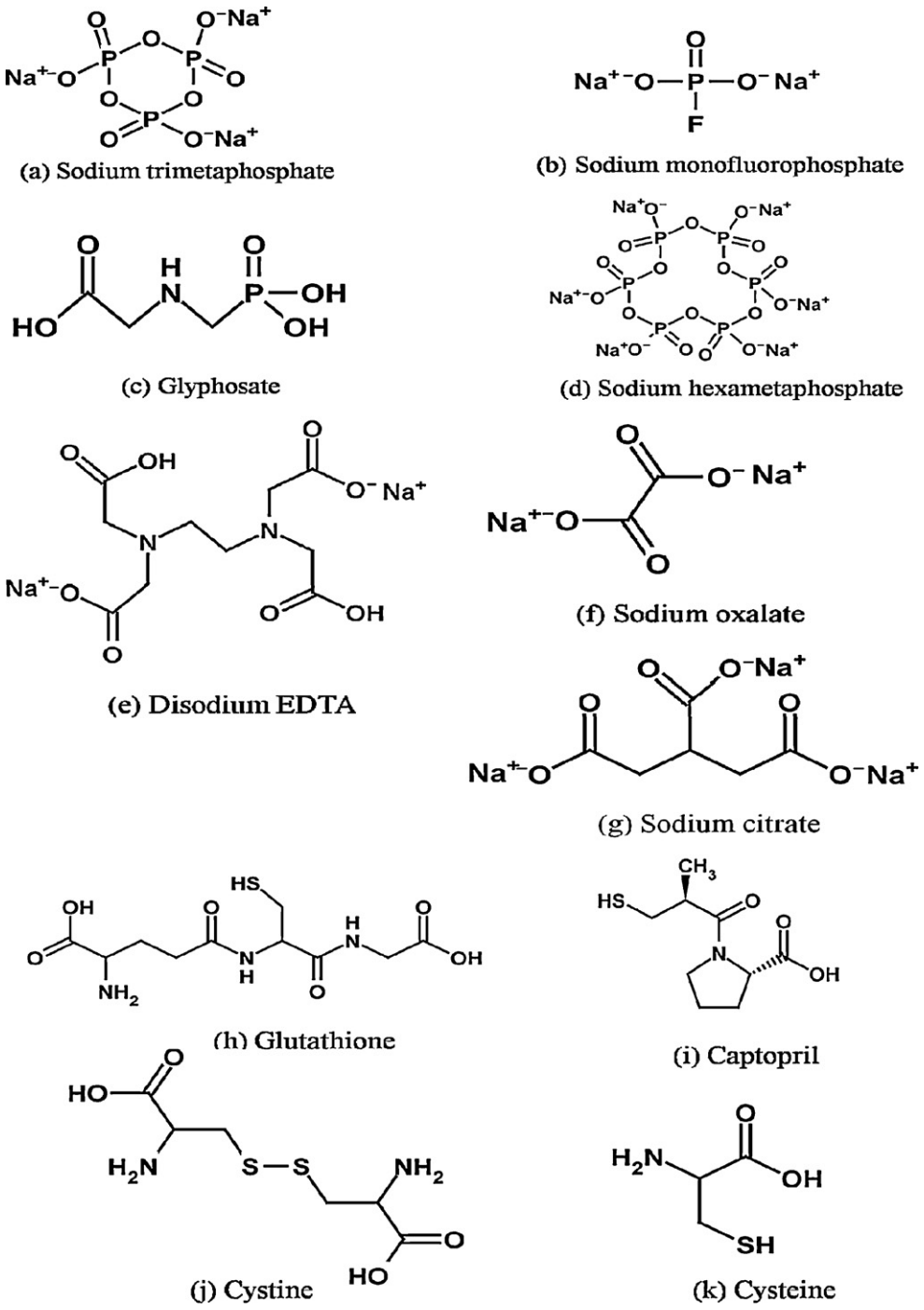

Fig. 1. Chemical structures of the studied phosphate compounds (a–d), polycarboxylates (e–g), and sulfhydryl derivatives (h–k).

injecting a volume of the reagent solution in a flowing stream of the sample. The rFI method has some advantages as it is very simple, requires very little or no sample preparation, decreases dispersion, improves analytical sensitivity, and consumes a small volume of the reagent. Several rFI methods were reported for direct determination of Al^{3+} in drinking water [19,20], dissolved oxygen [21], iodate and iodide in table salt [22], iron(III) using either chlortetracycline [23] or norfloxacin [24], and complexing agents such as EDTA, 1,2-cyclohexylenedinitrilotetraacetic acid, nitrilotriacetic acid, citrate, and pyrophosphate [25]. The complexing agents were determined by the acceleration of the redox reaction of Cu(II) with Fe(II) in the presence of neocuproine.

The main goal of this work is to show the versatility of the simple inexpensive reagent Fe(III)–salicylate for the indirect determination of carboxylate, phosphate, and sulfhydryl compounds (Fig. 1) using Fe(III)–salicylate exchange complexation through FI and rFI.

2. Experimental

2.1. Apparatus

An Agilent 8453 spectrophotometer was used for measurement of the absorbance to determine the wavelength of maximum absorbance and to optimize the pH. The FI manifold consisted of

a Dionex DX-120 HPLC pump with the appropriate reagent volume injected using a 1 mL disposable syringe. The purple complex was passed through a flow through cell in a Shimadzu SPD-6AV UV detector for continuous monitoring at 525 nm. A 50 cm long Teflon tubing of 0.5 mm I.D. was used as a reaction coil in the rFI procedures. For optimization procedures, a Waters 717 Autosampler and Waters Millipore M.45 pump were used together with a Kratos 757 Spectroflow detector. Data acquisition was done using SRI Peak Simple software.

2.2. Solvents and chemicals

All solvents and chemicals used in this work were of analytical grade obtained from Fisher Scientific (ferric nitrate, disodium EDTA dihydrate, and sodium citrate), Sigma (trimetaphosphate, glyphosate, cysteine and glutathione), Sigma–Aldrich (captopril), Johnson Matthey catalog (sodium hexametaphosphate and sodium monofluorophosphate), and Matheson Coleman & Bell (sodium oxalate). (Citroma)® syrup was purchased from Swan.

2.3. Procedures

For the offline reaction flow injection (oFI) method, aliquots equivalent to 0.034–2.725 μmol of sodium citrate were accurately transferred from their stock solution (340 μmol L^{-1}) and completed to volume with 100 μmol L^{-1} Fe(III)–salicylate pH 3 in a series of 25 mL volumetric flasks. Each solution was injected in a flowing steam of 100 μmol L^{-1} Fe(III)–salicylate pH 3 with absorbance recorded at 525 nm. To avoid the dilution effect, the volume taken of sample was kept constant in each prepared solution. For the rFI method, aliquots equivalent to 0.17–1.02 mmol of sodium citrate were accurately transferred from their stock solution (340 mmol L^{-1}) and completed to volume with water, pH adjusted to 3 with nitric acid, in a series of 250 mL volumetric flasks. Each solution was used as a flowing stream in which 3 mmol L^{-1} Fe(III)–salicylate pH 3 was injected and absorbance was recorded at 525 nm. To optimize the different FI parameters, the sensitivity was determined based on the slope of the analytical curve, built using four solutions of different concentration, each injected in triplicate. The analytical curves were obtained by plotting the peak area in area units (AU) against the concentration in μmol L^{-1} and the regression equation was derived.

3. Results and discussion

The offline reaction flow injection (oFI) method was based on the principle that if 20 μmol L^{-1} Fe(III)–salicylate solution is injected in a flowing stream of 20 μmol L^{-1} Fe(III)–salicylate, there should be no decrease in the absorbance and hence, no peak is observed. When the compound of interest is dissolved in 20 μmol L^{-1} Fe(III)–salicylate solution and then injected in a flowing stream of 20 μmol L^{-1} Fe(III)–salicylate, there will be a decrease in the absorbance with a magnitude equal to how much Fe(III)–salicylate is consumed in the interaction with the compound of interest which is, in turn, proportional to the concentration of the studied compound. On the other hand, rFI utilized the sample as a flowing stream in which Fe(III)–salicylate was injected. Sodium citrate was used for initial flow optimization in both oFI and rFI methods.

3.1. Optimization of the detection reaction

The kinetics of sodium citrate reaction with Fe(III)–salicylate was studied from 0 to 1200 s and it was found that the reaction was instantaneous with a rate of absorbance change of -7.95×10^{-5} and a standard deviation of 3.4×10^{-7}.

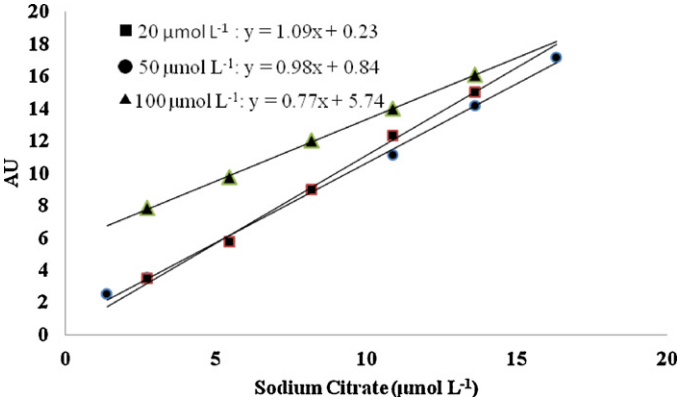

Fig. 2. Effect of Fe(III)–salicylate concentration on the sensitivity the oFI method using 20 (■), 50 (●) and 100 (▲) μmol L^{-1} Fe(III)–salicylate.

The effect of pH on Fe(III)–salicylate absorbance was studied by changing the pH from 1 to 3.5. The increase in pH led to an increase in the absorbance to a maximum at pH 3 with a reasonable plateau over one pH unit. Hence, pH 3 was chosen as optimum in the following procedures in both oFI and rFI methods.

In the oFI method, the concentration of the Fe(III)–salicylate complex in the flowing stream had significant effect on the sensitivity based on the difference in the slope of the analytical curves measured using 20, 50, and 100 μmol L^{-1} Fe(III)–salicylate complex concentrations. Fig. 2 shows that a 20 μmol L^{-1} Fe(III)–salicylate complex concentration gave the highest sensitivity. Using lower concentrations is possible but at the expense of the linearity range. Tables 1 and 2 show a comparison between the performance data, accuracy and precision of the two analytical curves using 20 μmol L^{-1} and 100 μmol L^{-1} Fe(III)–salicylate complex concentrations, respectively. The use of the 100 μmol L^{-1} Fe(III)–salicylate complex concentration gave a wider linearity range, and a better precision. In addition, the 100 μmol L^{-1} Fe(III)–salicylate was more robust against small changes in Fe(III)–salicylate concentration as compared to 20 μmol L^{-1} as the concentration.

In the rFI method, the effect of Fe(III)–salicylate concentration was studied in the range of 1–6 mmol L^{-1}. As shown in Fig. 3, the sensitivity improved with increasing concentration up to 3 mmol L^{-1}. Upon using higher concentrations of Fe(III)–salicylate, no further increase in the sensitivity was observed. Therefore, 3 mmol L^{-1} Fe(III)–salicylate concentration was chosen to avoid useless consumption of the reagent.

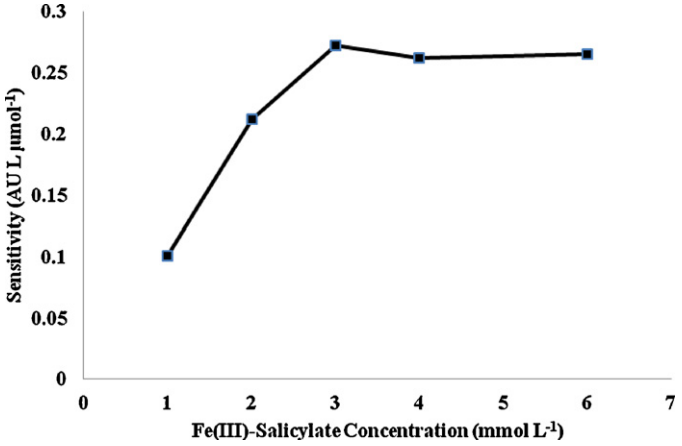

Fig. 3. Effect of Fe(III)–salicylate concentration on the sensitivity of the reverse flow injection (rFI) method.

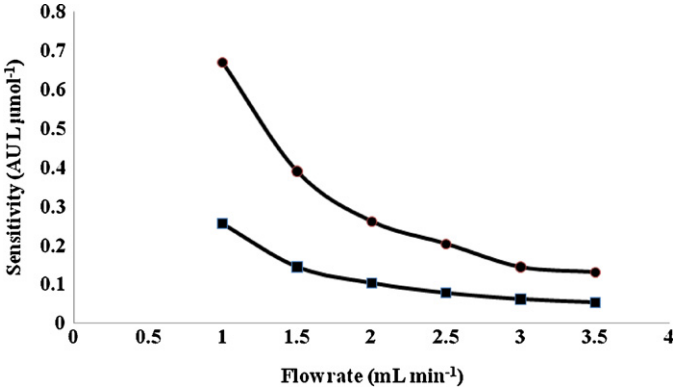

Fig. 4. Effect of flow rate on the sensitivity of the oFI (●) and the rFI (■) methods.

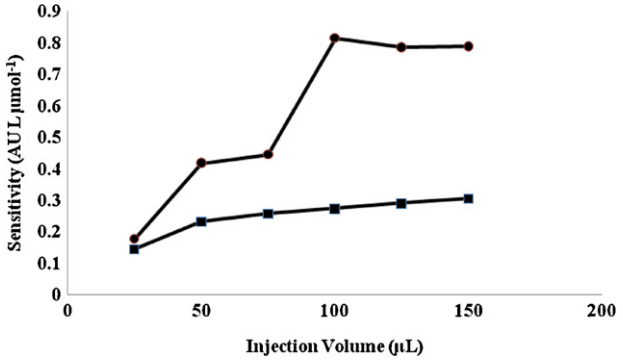

Fig. 5. Effect of injection volume on the sensitivity of the oFI (●) and the rFI (■) methods.

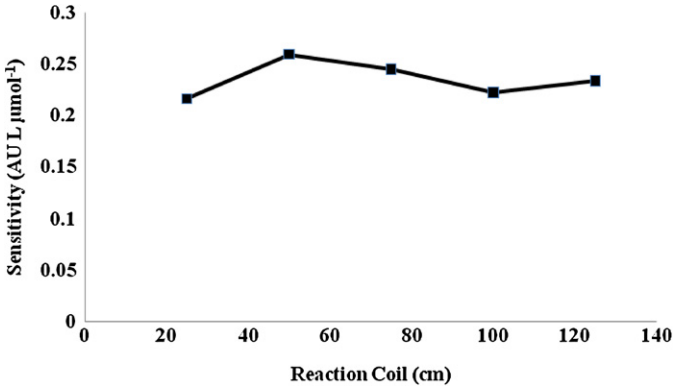

Fig. 6. Effect of reaction coil length on the sensitivity of the rFI method.

3.2. Effect of instrument parameters

The influence of the flow rate on the sensitivity in both oFI and rFI methods was studied. As shown in Fig. 4, the highest sensitivity in both the oFI and the rFI method was achieved when 1 mL min^{-1} flow rate was used. Lower flow rates do give rise to stronger signals but were avoided to ensure good sample throughput.

As shown in Fig. 5, the sensitivity of both methods was affected by the change in the injection volume. Injection volumes of 100 and 125 μL were chosen as optimum in the oFI and rFI methods, respectively.

Since the reaction is completed before injecting the sample in the oFI method, there was no need for a reaction coil and a short polymeric union connector was used instead. On the other hand, the reaction coil length was increased in the rFI method from 25 cm to 125 cm. As shown in Fig. 6, a reaction coil length of 50 cm gave slightly higher sensitivity, and hence it was regarded as the optimum length.

Table 1
Performance data of the offline reaction FI method for citrate.

Parameter	20 μmol L^{-1} Fe(III)–salicylate	100 μmol L^{-1} Fe(III)–salicylate
Concentration range (μmol L^{-1})	1.36–13.6	1.36–109
LOD (nmol L^{-1})	50	72
LOQ (nmol L^{-1})	167	239
Correlation coefficient	0.996	0.999
Slope (AU L μmol^{-1})	1.089	0.762
Intercept (AU)	0.232	5.739
S.D. (AU L μmol^{-1})	6.7×10^{-2}	1.2×10^{-2}

3.3. Analytical figures of merit

Using the proposed oFI method under the optimum conditions (Table 3), the linear calibration graph over the range (1.36–109 μmol L^{-1}) was established giving a regression equation of $y = 0.816x + 6.27$ ($r^2 = 0.995$) and a standard deviation of 5.1×10^{-2}. The limit of detection (LOD) and the limit of quantitation (LOQ) were calculated using the following equations:

$$\mathrm{LOD} = \frac{3N}{S}, \quad \mathrm{LOQ} = \frac{10N}{S}$$

where N is the standard deviation of the peak area in blank injection (five injections) and S is the slope of the calibration curve. The LOD and LOQ were found to be 57 and 189 nmol L^{-1}, respectively.

The same equations were applied to determine LOD and LOQ in the second proposed rFI method under the optimum conditions

Table 2
Accuracy and precision data for sodium citrate by the oFI method.

Parameter	20 μmol L^{-1} Fe(III)–salicylate			100 μmol L^{-1} Fe(III)–salicylate		
	Taken (μmol L^{-1})	Found (μmol L^{-1})	% Recovery	Taken (μmol L^{-1})	Found (μmol L^{-1})	% Recovery
Intra-day precision						
	8.16	8.04	98.46	13.60	13.60	100.03
	10.88	11.10	101.97	40.80	40.66	99.64
	13.60	13.60	99.97	108.81	109.40	100.55
Mean			100.13			100.07
% RSD			1.76			0.46
Inter-day precision						
	8.16	8.19	100.42	13.60	13.53	99.51
	10.88	11.00	101.13	40.80	41.06	100.63
	13.60	13.45	98.90	108.81	108.71	99.91
Mean			100.15			100.01
% RSD			1.14			0.57

Table 3
Summary of the optimum conditions for the proposed FI methods.

Variable	oFI		rFI	
	Range studied	Optimum value	Range studied	Optimum value
pH	1.0–3.5	3.0	1.0–3.5	3.0
Fe–salicylate concentration (mmol L^{-1})	0.02–0.1	0.1	1–6	3
Flow rate (mL min^{-1})	1.0–3.5	1.0	1.0–3.5	1.0
Injection volume (μL)	25–150	100	25–150	125
Reaction coil (cm)	–	–	25–125	50

Table 4
Performance data for citrate using 3 mmol L^{-1} Fe(III)–salicylate by reverse FI.

Parameter	Results
Concentration range (mmol L^{-1})	0.68–4.08
Limit of detection (μmol L^{-1})	21
Limit of quantification (μmol L^{-1})	70
Correlation coefficient	0.995
Slope (AU L μmol^{-1})	−0.291
Intercept (AU)	2213
S.D. (AU L μmol^{-1})	7.8×10^{-3}

shown in Table 3. The performance data for the rFI method is shown in Table 4. Although the rFI method is less sensitive than the oFI method, it consumes less reagents and requires no sample preparation. On the other hand, the oFI method offers advantages of higher sensitivity, higher throughput, and applicability to slow chemical reactions or reactions that require special conditions that cannot be conducted on line.

3.4. Interferences

The interference possibility of the excipients, saccharin, polyethylene glycol, and sucrose, in the pharmaceutical product (Citroma)® was studied. None of the tested inactive ingredients caused interference with citrate. The effect of other mono- and polycarboxylates was also examined. Monocarboxylates such as formate and acetate did not interfere but all the examined polycarboxylates (oxalate and EDTA) interfered.

3.5. Analysis of real samples

The accuracy and precision of the two proposed methods were assessed by spiking (Citroma)® with known amount of citrate and determining the amount recovered. The results were compared to a reference method [26] which was based on the photochemical decomposition of the Fe(III)–citrate complex to Fe(II) and measuring the catalysis of the chemiluminescent luminol reaction by the resultant Fe(II) in absence of added oxidant. The average % recovery was 100.73 and 100.69 for oFI and rFI methods, respectively compared to a 99.95% reported recovery for the reference method. Statistical comparison between our results and the reported % recovery of citrate synthetic samples was performed using Student's *t*-test at the 95% confidence level and there was no significant difference between the results obtained by the two developed methods and the reference method.

3.6. Method applicability to other polycarboxylates, phosphate, and sulfhydryl compounds

The versatility of this oFI indirect detection approach was checked by applying the oFI method to other polycarboxylates such as oxalate, and EDTA, phosphate compounds such as ortho-phosphate, trimetaphosphate, and hexametaphosphate, and sulfhydryl compounds such as cysteine. The analytical figures of merit for these tested compounds are shown in Table 5. As for the polycarboxylates, there was a direct relationship between the number of carboxylate groups and the sensitivity. This can be explained by the difference in mole ratio between the studied compounds which is 1:1 in case of Fe–EDTA [27,28], 2:3 in case of Fe–citrate [29], and 1:3 in case of Fe–oxalate complex [30]. However, that was not the case for the anionic phosphorous compounds. Hexametaphosphate with six phosphorus atoms had the highest sensitivity but trimetaphosphate had apparently lower sensitivity than monofluorophosphate. This could possibly be explained by the rigid cyclic structure of sodium trimetaphosphate. In spite of also being a cyclic structure, sodium hexametaphosphate showed higher flexibility due to the large ring size compared to sodium trimetaphosphate.

Glyphosate, a phosphorus and carboxyl containing compound, gave a slope close to the bidentate ligands, cysteine and oxalate. oFI and rFI studies of three glyphosate standard concentrations (59, 118 and 177 μmol L^{-1}) showed recoveries ranging from 99.3 to 100.6% with RSD values less than 1% ($n = 7$). As for the sulfhydryl containing compounds, only cysteine could displace salicylate from Fe(III)–salicylate complex while captopril, glutathione and cysteine could not. This can be explained by studying the structure of Fe(III)–cysteine complex which could form between ferric ion and the sulfhydryl group together with the hydroxyl group [31]. Glutathione lacks the hydroxyl group of cysteine due to the formed peptide bond while cysteine lacks the sulfhydryl group due to formation of disulfide bond. Although captopril has both sulfhydryl and hydroxyl groups, they are six atoms apart which means that they cannot represent two sites of attachments of a stable chelate. In case of cysteine, the sulfhydryl and the hydroxyl are three atoms apart, thus cysteine can form a six-membered stable chelate. The inability of glutathione, captopril and cystine to displace salicylate

Table 5
Performance data for other compounds using offline flow injection.

Compound	Range (μmol L^{-1})	*n*	Regression equation	r^2	LOD (nmol L^{-1})
EDTA	1–10	9	$y = 2.10x + 1.08$	0.997	22
Sodium oxalate	3–30	9	$y = 0.36x + 0.22$	0.995	130
Hexametaphosphate	1.3–6.5	7	$y = 4.22x + 0.21$	0.989	11
Monofluorophosphate	5–50	6	$y = 0.56x - 0.27$	0.986	82
Trimetaphosphate	13–92	7	$y = 0.24x - 0.25$	0.979	195
Glyphosate	30–207	7	$y = 0.33x + 6.02$	0.999	139
Cysteine	3–33	7	$y = 0.36x + 0.42$	0.998	129

n: number of points.

does not mean that they cannot form complexes with ferric ion, but it means that they could be weaker ligands than salicylate.

4. Conclusion

Two flow injection analysis methods were developed for determination of polycarboxylates, sulfhydryl, and phosphorous compounds using a Fe(III)–salicylate exchange complexation reaction. In the offline reaction flow injection (oFI) method, 100 μM Fe(III)–salicylate complex at pH = 3 was used as a flowing stream in which the sample, dissolved in 100 μM Fe(III)–salicylate, was injected. The relationship between the structure and the method sensitivity was optimized; the three studied polycarboxylate showed slopes differing according to number of carboxylate groups incorporated in the structure. The studied phosphates did not show the same relationship between the number of phosphate groups in the compound and the calculated slopes. The oFI method has advantage of indirect detection using a displacement reaction which offers selectivity for the method using simple instrumentation. This method is also preferred if the reaction is slow or complicated. The second method is reverse flow injection (rFI) with the sample as the running stream in which 3 mmol L^{-1} Fe(III)–salicylate complex was injected and the decrease in response with increased sample concentration was monitored. The two developed methods were successfully applied for the determination of spiked citrate in the commercial product (Citroma)® and an agreement with the reference method was obtained and verified by the Student's *t*-test at 95% confidence level. Future work will be directed toward Fe(III)–salicylate as an on- or post-column detection reagent for HPLC of carboxylates and phosphates.

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