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Sensor film for Vitamin C determination based on absorption properties of polyaniline

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Abstract

An analytical method based on the absorption changes of chemically polymerised polyaniline at 700 nm is proposed for the determination of Vitamin C. Vitamin C produces a polyaniline film reduction, originating changes in its absorbance proportional to the Vitamin C concentration. The optimum reaction conditions and the analytical characteristics have been studied. The linear response of the method ranged from 0.10 to 1.0 mg l^{-1} for a 6 min reaction time and from 1.0 to 8.0 mg l^{-1} for a 2 min reaction time. Reproducibility, expressed as the coefficient of variation, was 0.8% (6 min reaction time) and 2.3% (2 min reaction time) (n = 10). The method has been applied to Vitamin C determination in pharmaceutical preparations and commercial fruit juices. The results were compared with those obtained by the 2,6-dichlorophenolindophenol titration method (the AOAC Official Method) and no systematic errors were observed.

Keywords: Optical sensor film; Vitamin C; Polyaniline; Redox

1. Introduction

Vitamins are organic substances necessary for the metabolism, which cannot be produced in sufficient quantities by the human organism, and must therefore be obtained from food. Vitamin C (L-ascorbic acid) is a hydro soluble vitamin which plays an important role in preventing illnesses such as scurvy and the common cold. This vitamin is found in high concentrations in citric fruits, blackberries, melons, tomatoes, green peppers, cabbages and green vegetables [1,2].

Traditional methods for Vitamin C (Vit C) determination generally involve titration with an oxidising agent, since Vit C is easily oxidised to dehydroascorbic acid. Iodometric and 2,6-dichlorophenolindophenol titration (the AOAC Official Method) are time consuming and not useful for low analyte concentrations. New techniques have therefore been developed, including the HPLC [3–5], amperometric [6,7], spectrophotometric [8–10], and fluorometric [11–13] methods.

In the last few decades, numerous sensors for food yields have been developed [14,15]. Sensors respond well to the current requirements of the food industry being rapid and affordable methods for assuring the quality of products and process control. In the case of Vit C determination, several sensors have been developed mostly amperometric. One of the most stable systems has been developed by Ravi Shankaran et al. [16], who have designed a sol–gel composite electrode for the simultaneous determination of Vit C and dopamine with a detection limit of 2.8 mg l^{-1} for Vit C. The sensor keeps 91% of the activity after 20 days. Alternatively, O'Connell et al. [17] have developed an amperometric sensor for Vit C based on electropolymerised aniline getting a good detection limit (0.04 mg l^{-1}) but with a reproducibility of 5.1% (n = 60), expressed as the coefficient of variation.

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The sensor film described in this study is a new reagentless system for Vit C determination based on the changes in absorption properties because of the redox interaction with polyaniline. The main advantage of this sensor film is both the low detection limit and the good stability, together with the high reproducibility.

Polyaniline (PAn) has been one of the most intensively investigated conducting polymers during the last 15 years because of its good combination of properties, stability, price, ease of synthesis, treatment, etc. PAn exists in three well-defined oxidation states: leucoemeraldine, emeraldine and pernigraniline. In the leucoemeraldine state all the nitrogen atoms are amines, whereas in pernigraniline the nitrogen atoms are imines. The amine/imine ratio in emeraldine is ∼1. Moreover, emeraldine can be in its base or salt form, depending on the pH. Aniline polymerisation, which can be carried out electrochemically or chemically, results in the emeraldine form [18,19]. The four different forms of PAn are of different colour, and its absorption properties have therefore been used for the determination of analytes with acid–base or redox properties. Some recent examples, apart from pH determination [20,21], are ozone [22], ammonia [23,24] and sulphite [25] determination.

2. Experimental

2.1. Apparatus

Absorbance measurements were performed with a HP 8452A diode array spectrophotometer using a 1 cm path length conventional glass cuvette. A Crison 2001 pH meter was used to adjust solutions to the desired pH.

2.2. Reagents

The following solutions were used in the experiments.

Buffer solutions: 0.1 M phosphate solution at pH 2 (from solid KH_2PO_4 and HCl) and Clark-Lubs buffer (0.1 M KCl and concentrated HCl) at pH 1.

Vitamin C solutions: 5 mg of L-ascorbic acid (Sigma A1417) were dissolved in 10 ml of phosphate buffer at pH 2. Other solutions were prepared by further dilution in phosphate buffer. These Vitamin C solutions were kept in darkness and used in the 4 h subsequent to its preparation.

Iron(III) solution: 48.66 g of $FeCl_3{\cdot}H_2O$ (Merck 1.03943.0250) were dissolved in 100 ml of bidistilled water. This solution (1.8 M, pH 1) was used for PAn film preparation. For film regeneration after reaction with Vit C, a more diluted solution (5×10^{-5} M) was prepared using Clark-Lubs buffer at pH 1.

Aniline solution: a 0.16 M solution was prepared by diluting 375 μl of the commercial reagent (Sigma A9880) in 25 ml of bidistilled water.

Polyester film of 75 μm thickness was supplied by DuPont de Nemours & Co. (Luxembourg).

2.3. Procedure

2.3.1. Preparation of PAn films

Twenty-five millilitres of aniline solution were added to a 50 ml glass beaker and stirred. Twenty-five millilitres of iron (III) chloride 1.8 M were added immediately and mixed for 30 s (*the pH value of the polymerisation solution was 1*). Four polyester films (1.3 cm × 4.5 cm) were placed in the solution. Thin films of PAn were formed on the polyester film (previously cleaned with ethanol and water) after 30 min polymerisation time and continuous stirring. In order to stop the polymerisation reaction, the PAn films were generously washed with bidistilled water. When not in use, the films were stored at 4 °C in plastic cuvettes (1 cm × 1 cm) containing phosphate buffer at pH 2.

2.3.2. Measurement procedure

Before the reaction, the absorbance value at 700 nm of the PAn film was measured placing the film crossways in a conventional glass cuvette filled with phosphate buffer at pH 2 ($A_{700\,nm,0\,min}$). The reaction between the film and the Vit C solution was then carried out during 2 or 6 min, depending on the Vit C concentration range. After generous washing in a new phosphate buffer solution, the absorbance value of the film at 700 nm was measured ($A_{700\,nm,2/6\,min}$) in the former buffer solution. The relationship between both values expressed as $A_{700\,nm,2/6\,min}/A_{700\,nm,0\,min}$ was used as the analytical parameter.

3. Results and discussion

The PAn film preparation procedure was optimised by the authors in a previously published work [25]. As has been mentioned, emeraldine is the PAn form resulting from chemical polymerisation of the aniline monomer. In this case, the PAn was mainly in the emeraldine salt form because of the pH of the polymerisation reaction (pH 1). When Vit C was present, a redox process took place and the oxidation degree of the film gradually decreased, the emeraldine salt form being reduced to the leucoemeraldine form, producing changes in the absorption properties of the PAn film dependent on the Vit C concentration (Fig. 1) and the reaction time.

3.1. Reversibility of the reaction

Once exposed to Vitamin C, the reduced PAn films did not return to their initial value. This fact was observed after the films were kept overnight both in phosphate buffer at pH 2 or in bidistilled water. Only a partial reversibility to the initial spectrum of the emeraldine form (depending on the pH of the regeneration solution) of the PAn film was obtained. Consequently, a study of the reversibility of the reaction was carried out in order to regenerate PAn films. The results are shown in Fig. 2. Considering the re-oxidation of the PAn film by the oxygen present in the buffer solution as a possible reason for

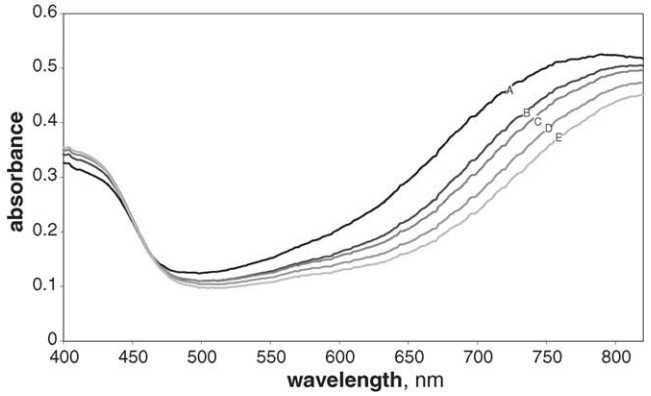

Fig. 1. Absorption spectra of PAn film before reaction (A) and after different reaction times with Vitamin C (4.0 mg l^{-1}): (B) $t_{reaction}$ = 1 min; (C) $t_{reaction}$ = 2 min; (D) $t_{reaction}$ = 4 min; (E) $t_{reaction}$ = 6 min.

the partial regeneration, the starting point was to study the PAn film regeneration with oxygen. A reduced PAn film was placed in a phosphate buffer solution while oxygen was being bubbled. Although the regeneration was better than in the case of non-oxygenated buffer, total reversibility was not observed after 2 h of oxygen bubbling. Regeneration of the PAn film in air was also studied. As can be seen in Fig. 2, after exposure of the film to air for 1 h, the effect was too strong because the oxidation did not stop at the emeraldine form, but went on to the pernigraniline form. Exposure of the film to the air could be useful for PAn regeneration provided there is continuous monitoring to stop the exposure at the right point. Another approach was to regenerate using an oxidant. The same oxidant was used as for the polymerisation step to avoid involving new chemicals, iron(III) chloride solutions at pH 1 in different concentrations. Highly concentrated solutions resulted in excessive oxidation of the PAn (see in Fig. 2 the effect of a solution 5×10^{-3} M), but excellent results were obtained for an iron(III) chloride concentration of 5×10^{-5} M. In this case, total regeneration was observed after a few minutes without excessive oxidation of the emeraldine form, even when the film was kept for several hours in the regeneration solution. Although the regeneration time depended on the degree of reduction of the PAn film, that is of the Vit C concentration, 8 min was found to be the maximum required time for the regeneration when reaction was carried out with a Vit C concentration of 8.0 mg l^{-1} (maximum value of the linear range). To avoid continuous monitoring of the regeneration process and to ensure total regeneration, 10 min was used as the regeneration time irrespective of the Vit C concentration in the reaction. After that, the films were stored in the previously used phosphate buffer solution at pH 2.

3.2. Analytical parameter

Absorption spectra of a PAn film before and after different reaction times are shown in Fig. 1. Three different aspects were studied in order to define an analytical parameter: the wavelength, the reaction time and the kind of parameter.

As can be seen in Fig. 1, the most significant changes in absorbance occurred between 700 and 740 nm. Consequently, absorbance changes at different reaction times and Vit C concentrations (from 0.10 to 25 mg l^{-1}) were studied at 700, 720, and 740 nm. The decrease in absorbance for three different Vit C concentrations at different reaction times is shown in Table 1. The results obtained showed that the relation between the parameter and Vit C concentration was linear in all cases. However, the most sensitive wavelength was 700 nm, which was therefore chosen as the optimum.

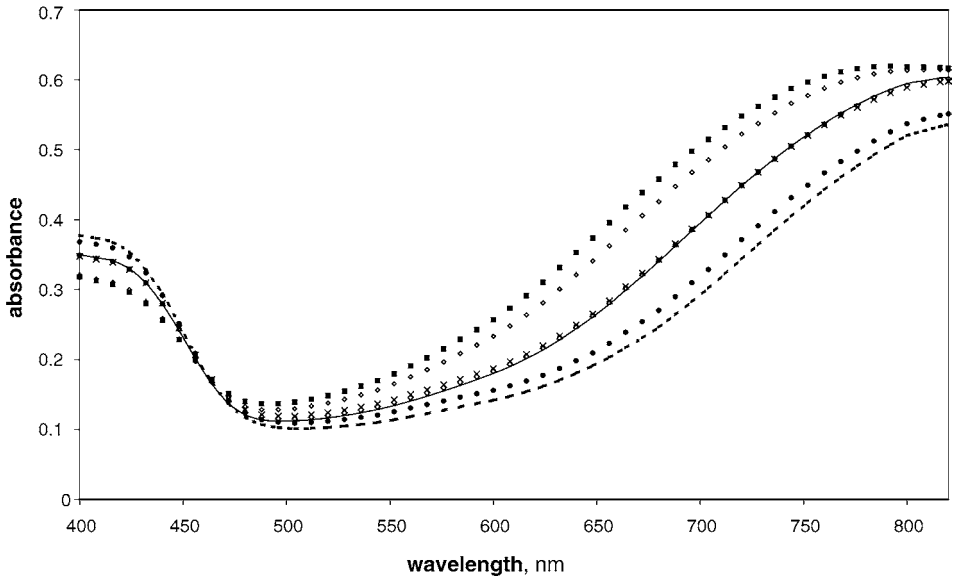

Fig. 2. Absorption spectra of a PAn film for various regeneration methods: (—) before reaction; (- - -) after reaction (2 min, [Vit C] = 5.0 mg l^{-1}); (●) regeneration after 2 h bubbling O_2; (□) regeneration after 1 h in air; (■) regeneration after 10 min in $FeCl_3$, 5×10^{-3} M; (×) regeneration after 10 min in $FeCl_3$, 5×10^{-5} M; (◯) regeneration after 2 h in $FeCl_3$, 5×10^{-5} M.

Table 1
Absorbance decreases at 700, 720 and 740 nm for different reaction times and Vit C concentrations

[Vit C] (mg l^{-1})	$-\Delta$Abs								
	$t_{reaction}$ = 1 min			$t_{reaction}$ = 2 min			$t_{reaction}$ = 6 min		
	700 nm	720 nm	740 nm	700 nm	720 nm	740 nm	700 nm	720 nm	740 nm
0.40	0.0041	0.0025	0.0005	0.0070	0.0048	0.0021	0.0172	0.0131	0.0079
1.0	0.0171	0.0141	0.0102	0.0265	0.0219	0.0169	0.0476	0.0406	0.0315
4.0	0.0803	0.0700	0.0583	0.1073	0.0976	0.0823	0.1795	0.1755	0.1593

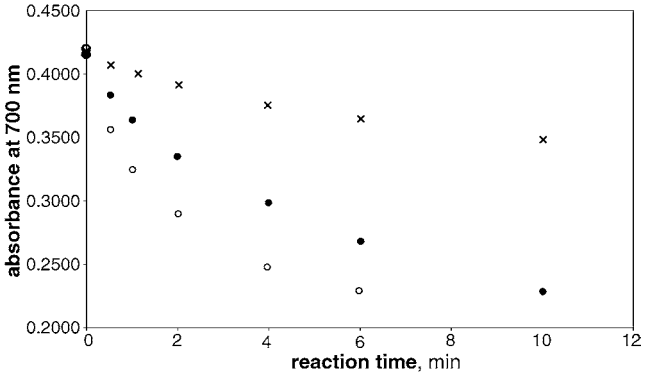

Fig. 3. Absorbance value at 700 nm at different reaction times for several Vit C concentrations: (×) [Vit C] = 1.0 mg l^{-1}; (●) [Vit C] = 3.0 mg l^{-1}; (○) [Vit C] = 5.0 mg l^{-1}.

Secondly, the reaction time was studied. Fig. 3 shows the absorbance value at 700 nm at different reaction times for several Vit C concentrations. As can be seen, the most significant changes occur within the first seconds of reaction. However, the range of Vit C concentration, which the method could be applied to, depended on the reaction time selected. Absorbance changes were established at different reaction times (from 20 s to 10 min) for different Vit C concentrations (between 0.10 and 25 mg l^{-1}). Table 2 shows the linear range between the absorbance decrease and Vit C concentration for some of the reaction times studied and linear fitting in all cases. Reaction times less than 1 min are not shown because of the unsatisfactory regression coefficient resulting from the irreproducibility associated with these short times. As can be seen, the reaction time had two other different effects: on the sensitivity and on the linear range of the method. Taking both into account together with the time involved in the measurements, a reaction time of 6 min was selected for Vit C concentrations lower than 1 mg l^{-1}. For Vit C concentrations higher than 1 mg l^{-1}, the reaction time chosen was 2 min.

Table 2
Linear behaviour of absorbance decrease (700 nm) and Vit C concentration at different reaction times

Reaction time	Linear range (mg l^{-1})	Linear fitting
1 min	0.40–10	0.0171[Vit C] + 0.0021, r = 0.994
2 min	0.30–8.0	0.0248[Vit C] + 0.0018, r = 0.997
4 min	0.20–6.0	0.0357[Vit C] + 0.0023, r = 0.995
6 min	0.10–4.0	0.0465[Vit C] + 0.0012, r = 0.996
10 min	0.10–3.0	0.0638[Vit C] + 0.0023, r = 0.997

Finally, the best analytical parameter was chosen for a wavelength of 700 nm and the selected reaction times. Three options were studied: (i) $A_{700\,nm,0\,min}$–$A_{700\,nm,2/6\,min}$; (ii) $A_{700\,nm,0\,min}/A_{700\,nm,2/6\,min}$; and (iii) $A_{700\,nm,2/6\,min}/A_{700\,nm,0\,min}$, where $A_{700\,nm,0\,min}$ and $A_{700\,nm,2/6\,min}$ were the absorbance values at 700 nm before reaction and after 2 or 6 min reaction time, respectively. The linear range and calibration curves obtained in all cases (according with the reaction time selected for each concentration range) are shown in Table 3. $A_{700\,nm,0\,min}/A_{700\,nm,2/6\,min}$ was discarded because the linear range was shorter than for the other two parameters. $A_{700\,nm,0\,min}$–$A_{700\,nm,2/6\,min}$ and $A_{700\,nm,2/6\,min}/A_{700\,nm,0\,min}$ showed similar linear responses. Not only was the regression coefficient slightly better for the latter, but it also showed higher sensitivity. $A_{700\,nm,2/6\,min}/A_{700\,nm,0\,min}$ was therefore chosen as the optimum analytical parameter.

3.3. Optimisation of the pH

The value of the analytical parameter was obtained when the reaction was carried out at different pH values (see Fig. 4). Since Vit C is unstable at weak acid and basic pHs, measurements were carried out immediately after preparation of the solutions. As can be seen, changes in the absorbance values of PAn films with Vit C concentrations decrease at pH values higher than 5. Apart from the parameter value, Vit C stability must also be taken into account. At no acid pH, Vit C is easily

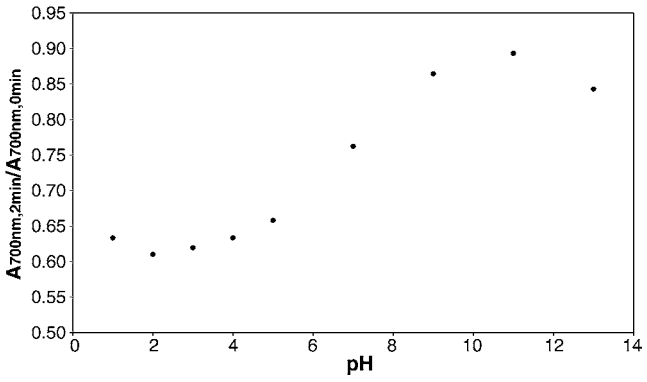

Fig. 4. pH effect on the analytical parameter ([Vit C] = 4.6 mg l^{-1}; $t_{reaction}$ = 2 min).

Table 3
Linear range and calibration curve for different analytical parameters

Parameter	$t_{reaction}$ = 2 min		$t_{reaction}$ = 6 min	
	Linear range (mg l^{-1})	Linear fitting	Linear range (mg l^{-1})	Linear fitting
$A_{700\,nm,0\,min}$–$A_{700\,nm,2/6\,min}$	1.0–8.0	0.0238[Vit C] + 0.0073, r = 0.997	0.10–1.0	0.0515[Vit C] − 0.0038, r = 0.9998
$A_{700\,nm,0\,min}/A_{700\,nm,2/6\,min}$	1.0–6.0	0.1109[Vit C] + 0.936, r = 0.995	0.10–1.0	0.1401[Vit C] + 0.987, r = 0.9995
$A_{700\,nm,2/6\,min}/A_{700\,nm,0\,min}$	1.0–8.0	−0.0633[Vit C] + 0.993, r = 0.998	0.10–1.0	−0.1239[Vit C] + 1.010, r = 0.9999

oxidised by the oxygen present in the solution. The degree of stability of Vit C (5000 mg l^{-1}) at different pH's was studied by absorption. After 5 h, more than 20% of the Vit C content had decreased at pH 4. This value decreased to 3% at pH 3 and was insignificant at pH 1 and 2. Since loss of *Vit* C over time is higher for those solutions with lower Vit C concentration [2], pH 3 was discarded in order to guarantee optimum stability during every work session. Taking into account both the analytical parameter value and the Vit C stability, pH 2 was chosen as the optimum.

3.4. Analytical characteristics

Fig. 5 shows the variation of the analytical parameter with the Vit C concentration in optimum conditions for both the 2 and 6 min reaction times. As can be seen, the linear response between the analytical parameter and the Vit C concentration (taking into account the concentration range used for each reaction time) ranged from 0.10 to 1.0 mg l^{-1} when the reaction time was 6 min and from 1.0 to 8.0 mg l^{-1} in the case of 2 min. The equations of the linear graphs using the least square method are given in Table 3. These conditions have been selected in order to improve the analytical characteristics of the method. However, as have been showed in Table 2, the linear range for each reaction time could be enlarged, if necessary.

Table 4
Tolerance to different redox compounds in the determination of Vitamin C

Compound added	Tolerance ratio
Sulphite	0.2
Thiosulphate	0.3
Fe(III)	>10[a]
Hydrogen peroxide	>100[a]
Peroxodisulphate	0.1

[a] Maximum ratio tested.

The reproducibility, expressed as the coefficient of variation, was 0.8% (n = 10) at a Vit C concentration of 0.50 mg l^{-1} ($t_{reaction}$ = 6 min) and 2.3% (n = 10) at 4.0 mg l^{-1} ($t_{reaction}$ = 2 min).

The film lifetime was studied for more than three months, measurements being taken four times a day (more than 200 measurements in total). Both the absorption spectra and the analytical parameter were similar in all the measurements (the coefficient of variation was 0.5% (n = 100) at a Vit C concentration of 0.50 mg l^{-1} ($t_{reaction}$ = 6 min) and 2.1% (n = 100) at 4.0 mg l^{-1} ($t_{reaction}$ = 2 min)). No sensitivity loss was observed during this time.

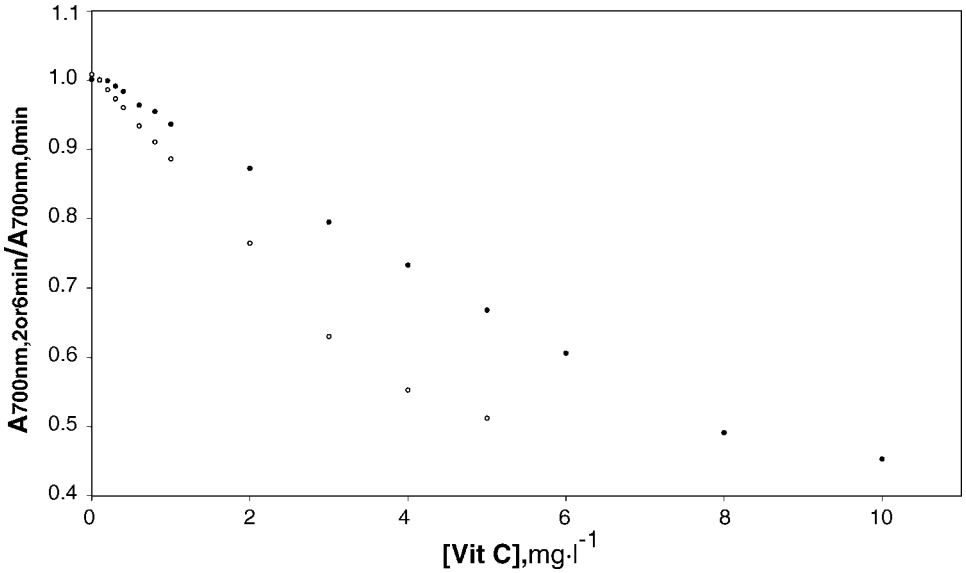

Fig. 5. Variation of the analytical parameter with the Vit C concentration in optimum conditions for two different reaction times: 2 min (●) and 6 min (○).

Table 5
Comparison of Vitamin C concentration found in different samples determined with PAn film and with the Official Method of Analysis (2,6-dichlorophenolindophenol titration), and results of recovery studies

Sample	Vit C nominal content	Vit C found reference method[a]	Vit C found proposed method[a]	Percentage recovery[a]
Cebion	500 mg per sachet	500.9 ± 1.7	502 ± 10	100.3 ± 3.8
Redoxon	1000 mg per tablet	1005.0 ± 4.0	1006 ± 22	99.8 ± 3.0
Efferalgan C	200 mg per tablet	194.6 ± 0.5	209 ± 12	110.0 ± 3.8
Aspirine C	240 mg per tablet	226.5 ± 1.7	224.2 ± 9.5	95.1 ± 3.3
Commercial pineapple juice		58.88 ± 0.16	61.0 ± 4.1	100.2 ± 6.0
Commercial orange juice		78.66 ± 0.41	82.3 ± 1.5	108.0 ± 4.3

[a] Mean ± S.D. (n = 3).

3.5. Application to real samples: study of interference

Since the response of PAn films with Vit C is due to a redox reaction, a study of the cross sensitivity of the film to the most common compounds with redox properties was carried out. Taking into account redox compounds present in real samples together with what is defined as interfering in the AOAC Official Method, the film response to sulphite, thiosulphate, Fe(III), hydrogen peroxide, and peroxodisulphate was studied under the conditions described. PAn films showed a similar response to compounds with reduction properties as to Vit C, although there were changes in the sensitivity (sulphite and thiosulphate sensitivity decreased by 50% and 75% compared to Vit C, respectively). Medium-oxidant compounds, Fe(III) and hydrogen peroxide, did not produce changes in the PAn spectrum. On the other hand, peroxodisulphate produced changes directly contrary to those produced by reductant compounds. In all the cases studied, when absorption changes were produced, total reversibility of the PAn film was possible.

The response of the PAn film to Vit C in the presence of these compounds was also studied. The tolerance ratio of each foreign species was taken as the largest analyte:Vit C molar ratio that altered the value of the analytical parameter obtained for a Vit C solution free of interference by more than 5%. The results are shown in Table 4. The most surprising result came from Fe(III), the compound used for PAn film regeneration which, however, did not produce interference during the reaction with Vit C. The reaction time was slower than the regeneration time, which would justify a decrease but not a total absence of reaction. An experimental study provided an explanation for this behaviour: the redox properties of the Fe(III) suffered a significant decrease when the pH was changed from 1 (regeneration pH) to 2 (reaction pH).

The method was applied to the determination of Vit C in pharmaceutical formulations and commercial fruit juices. The method potential was evaluated by comparing the results with a reference method based on the reaction of Vit C with 2,6-dichlorophenolindophenol titration (the AOAC Official Method) and also by recovery studies using the standard addition method. Prior to determination with the PAn film, the samples were dissolved and diluted to the appropriate concentration with phosphate buffer at pH 2. The results are shown in Table 5. Each value is the mean of three determinations. The standard deviation value of the proposed method was higher than that of the Official Method, but was in the range of typical values of relative standard deviations for instrumental methods (3–4%). When a t-test (P = 99%) was applied to the results obtained with PAn films and the Official Method, no significant differences were observed between the methods. Adding to the samples a Vit C quantity equivalent to that initially found in the samples (Table 5) carried out recovery studies. These results demonstrate the possibility of determining Vit C by the method recommended in this work.

4. Conclusions

Changes in the PAn film spectrum were used for Vitamin C determination. The method was successfully validated and applied to pharmaceutical formulations and commercial fruit juices. The method here described is simple, rapid, reproducible and sensitive (the detection limit is 500 times higher than for the 2,6-dichlorophenolindophenol titration method). Moreover, neither sample pre-treatment nor reagents (apart from buffer solution) are required for the determination. Film fabrication is also cheap, simple, rapid and reproducible. In addition, PAn films offer total reversibility and long lifetimes (more than 200 measurements and 3 months). These characteristics make this system a very good alternative for routine analysis of Vit C.

This promising methodology could be used for the design of methods for determining other analytes with reduction properties or strong oxidants.

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