Determination of Iron in Dietary Supplements by Voltammetric Analysis at an Iodine-Coated Polycrystalline Platinum Electrode

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An iodine-coated polycrystalline platinum electrode was applied to analysis of iron in dietary supplements. The developed method is based on scanning the potential of the iodine-coated polycrystalline platinum electrode between the hydrogen evolution limit (-0.25 V) and a potential lower than the threshold of iodine desorption from the platinum surface (ca. +0.80 V). An anodic peak centered nearly at 0.56 V is assigned to Fe(II) oxidation to Fe(III). The anodic peak current (i_p) showed an excellent linearity ($R^2 = 0.995$) with the concentration of Fe^{2+} within a concentration range from 4-500 ppm Fe. The anodic peak current, as expected for a diffusion controlled process showed a linear relationship with the square root of the scan rate ($R^2 = 0.999$). The limit of detection (based on S/N = 3) for the developed method is 2.34 ppm while the limit of quantitation (based on S/N = 10) is 7.8 ppm. The effect of potential interferences like calcium, magnesium, zinc, selenium, copper, manganese, chromium, molybdenum, vanadium was investigated. Silver and copper were the only ones among the investigated elements which showed resolved peaks from those of Fe (II) within the accessible potential window of the iodine-coated platinum electrode. Analysis of real samples and application of statistical tests to the results indicated the absence of systematic error in the results and the validity of the null hypothesis, i.e., there is no significant difference between the nominal values reported by the manufacturers and our results at p=0.05.

1. INTRODUCTION

Determination of iron in dietary supplements is of prime importance because of its connection with human health [1]. Many methods in the past decades have been developed for iron in dietary supplements [2-5]. The recent trend, however, in chemical analysis is the search for simple green methods, i.e., methods that require minimum or no chemical reagents with simple methodologies and

simple instrumentation. Electrochemical methods to a large extent meet these requirements. In electrochemical techniques where solid electrodes are used, the electrodes themselves are the active sites where heterogeneous chemical reactions occur. Noble metallic electrodes can be used for several years sometimes with minimum sample pretreatment and few reagents which fulfill the criteria of green chemical analysis. The problem with noble solid electrodes, however, is their susceptibility towards adsorption which opened the avenues towards modification of solid electrodes [6].

Iodine-coated platinum electrodes present a model for modification of the highly reactive platinum electrode. An adsorbed monolayer of iodine at a platinum surface converts the highly reactive platinum electrode to a remarkably passive electrode [7]. Iodine desorbs from platinum surfaces by electrooxidation of the adsorbed iodine [8] or electroreduction by scanning the electrode potential in the hydrogen adsorption/desorption region in alkaline solutions [8]. Iodine also can be electrochemically replaced by other adsorbates like carbon monoxide which is known to replace the adsorbed iodine quantitatively from platinum surfaces [9]

Iodine-coated platinum electrode was used for quantification of some species in aqueous solutions with and without further modification. An iodine-coated platinum electrode furtherly modified with quaternized poly(4-vinylpyridine), qPVP by Cox and Kulesa for analysis of nitrite[10]. Hourani and co-workers have used the iodine-coated platinum electrode for determination of silver(I), copper(II) [7] indirect determination of nitrogen oxides [11] and indirect determination of sulfur dioxide [12] in the atmosphere and hydroquinone in pharmaceutical preparations [13].

The simplicity of preparation of the iodine-coated platinum electrode and the simplicity of determination procedure, absence of the need for environment unfriendly chemical reagents, and the simplicity of instrumentation were all tempting to undertake the present work. This work was undertaken with an objective of extending the voltammetric analysis at iodine-coated platinum electrode to iron in dietary supplements.

2. EXPERIMENTAL

2.1 Instruments, cell and materials

A 372A potentiostat (EG & G, Princeton Applied Research) interfaced to a computer via GPIB (IEEE) interface and operated by M270 software was used for experimental control and data acquisition. An H-shape home-made electrochemical cell with multiple inlet/outlet 5/13″ ground joints for gas purging, gas blanketing and solutions delivery and drain was used for voltammetric measurements. The two compartments of the cell were separated by a fine glass frit. One compartment of the cell was used for housing the working electrode while the other was used for housing the reference and the auxiliary electrodes. The working electrode was a 1.0 mm polycrystalline platinum wire purchased from Aldrich (99.99% minimum purity certified reagent) rounded at one end into a U-shape to make a mark when immersed under the surface of the solution for reproducing a consistent surface area. The auxiliary electrode was a spiral-shape platinum wire (Aldrich, certified 99.99%

minimum purity) inserted in a glass jacket while the reference electrode was a home-made silver/silver chloride electrode in 1.0 M KCl solution.

All the materials used in the present work were analytical grade reagents and used as received from the suppliers without further purification. Sulfuric acid (95-97 %) was supplied by Merck, potassium iodide was purchased from Sigma-Aldrich and iron standards were purchased from Park Scientific (UK). Nitrogen gas G5 grade (99.999%) minimum purity was supplied from The Jordanian Gas Company.

2.2 Experimental procedures

Every experiment was commenced by reproducing the cyclic voltammogram of polycrystalline platinum where reproduction of the cyclic voltammogram of polycrystalline platinum was taken as a criterion of cleanliness of the electrochemical system including the electrodes, the solutions, and the purging gas.

The details of coating the platinum surface with iodine is described elsewhere [13]. Briefly, the platinum electrode was brought in contact with a supporting electrolyte, 0.50 M H_2SO_4 solution containing 1.0×10^{-2} M KI. The electrode was left to equilibrate with the solution for five minutes under open-circuit conditions. The electrode was then extensively rinsed with the iodine-free 0.50 M H_2SO_4 solution, and the cyclic voltammograom was recorded between -0.25 V and 0.80 V in an iodide-free 0.50 M H_2SO_4 solution. The absence of any voltammetric features except the charging current is a manifestation of a complete coating of platinum electrode with iodine.

The dietary supplement samples were collected from Jordanian local drug stores in the form of tablets and capsules. Three brands of dietary iron supplements were analyzed for their iron content. These brands namely were Ferrous gluconate, Glucofer, and Fefol. A sample of each brand was treated separately where a tablet or a capsule was ground into a fine powder and dissolved in 50.00 mL of 0.50 M H_2SO_4 solution. The solution was sonicated for 30 min., and left to equilibrate for 30 minutes. The solution was placed in a 100.00 mL volumetric flask and the flask was filled to the mark with 0.50 M H_2SO_4 solution. The solution was furtherly sonicated for 15 minutes for homogenization. . A 15.00 mL aliquot of this solution was diluted to 25.00 mL with 0.50 M H_2SO_4 and placed in the working electrode compartment. Volta metric analysis was conducted at the aforementioned iodine-coated electrode in a limited potential window where the san was initiated from -0.250 V and terminated at 0.800 V.

3. RESULTS AND DISCUSSION

3.1 Analytical parameters of the developed method

Figure 1 shows the cyclic voltammogram of a polycrystalline platinum electrode along with the voltammogram displayed by the same electrode after coating with iodine. The voltammogram for the iodine-coated platinum electrode shows complete absence of the well-known voltammetric features

due to hydrogen adsorption/desorption and oxygen adsorption/desorption at the polycrystalline platinum electrode.
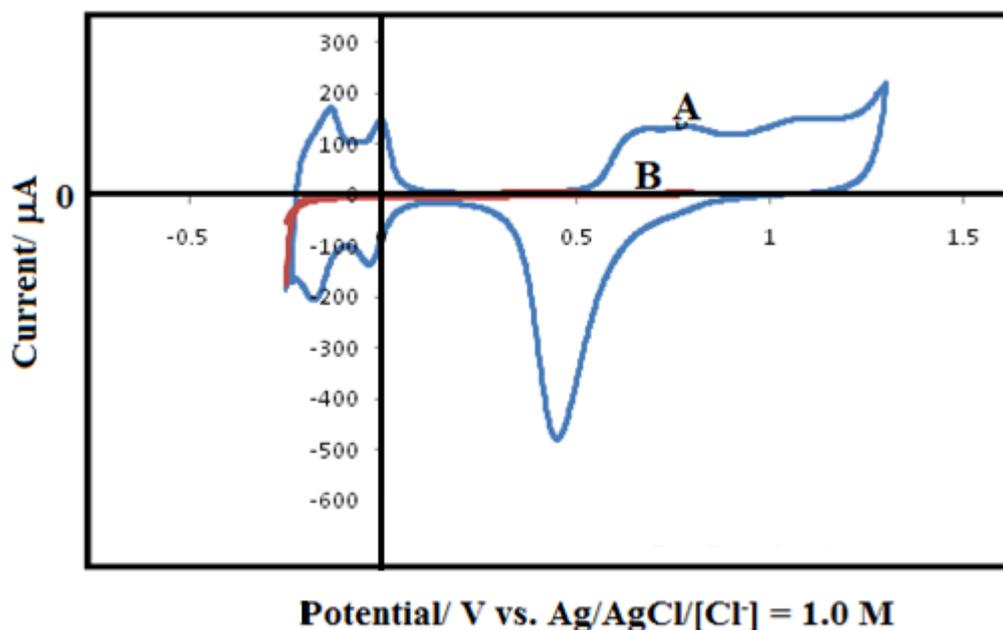
Figure 1. The cyclic voltammogram of (A) polycrystalline platinum electrode and (B) the same electrode after adsorption of iodine from 0.50 M +1.0x10^{-2} M KI solution. Both i-E scans were recorded in iodine-free 0.5 M H$_2$SO$_4$ at a scan rate of 100 mV/s.
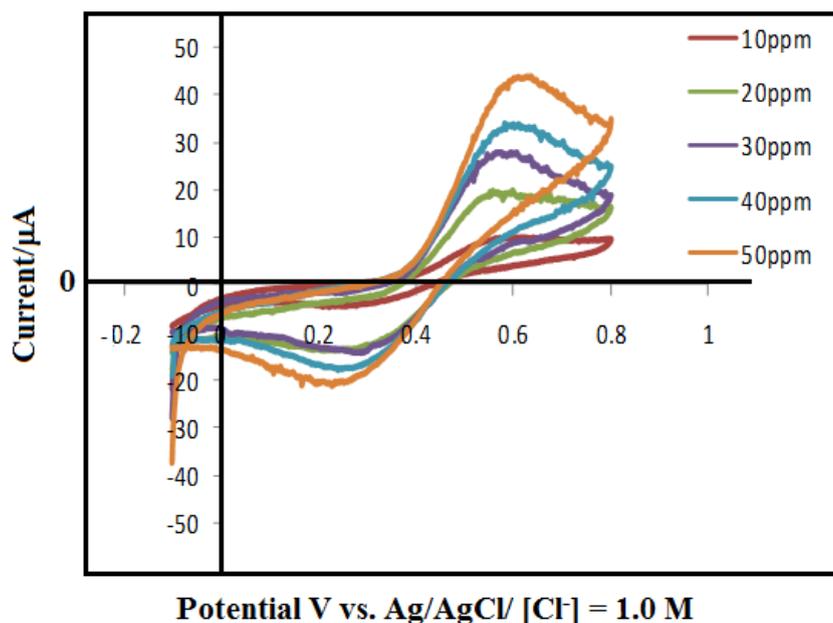
Figure 2. Cyclic voltammograms of an iodine-coated electrode in 0.5M H$_2$SO$_4$ solution containing (—)10ppm Fe(II) (—)20ppm Fe(II) (—)30ppm Fe(II) (—)40ppm Fe(II) (—)50ppm Fe(II). All the scans were recorded at a scan rate of 100 mV/s.
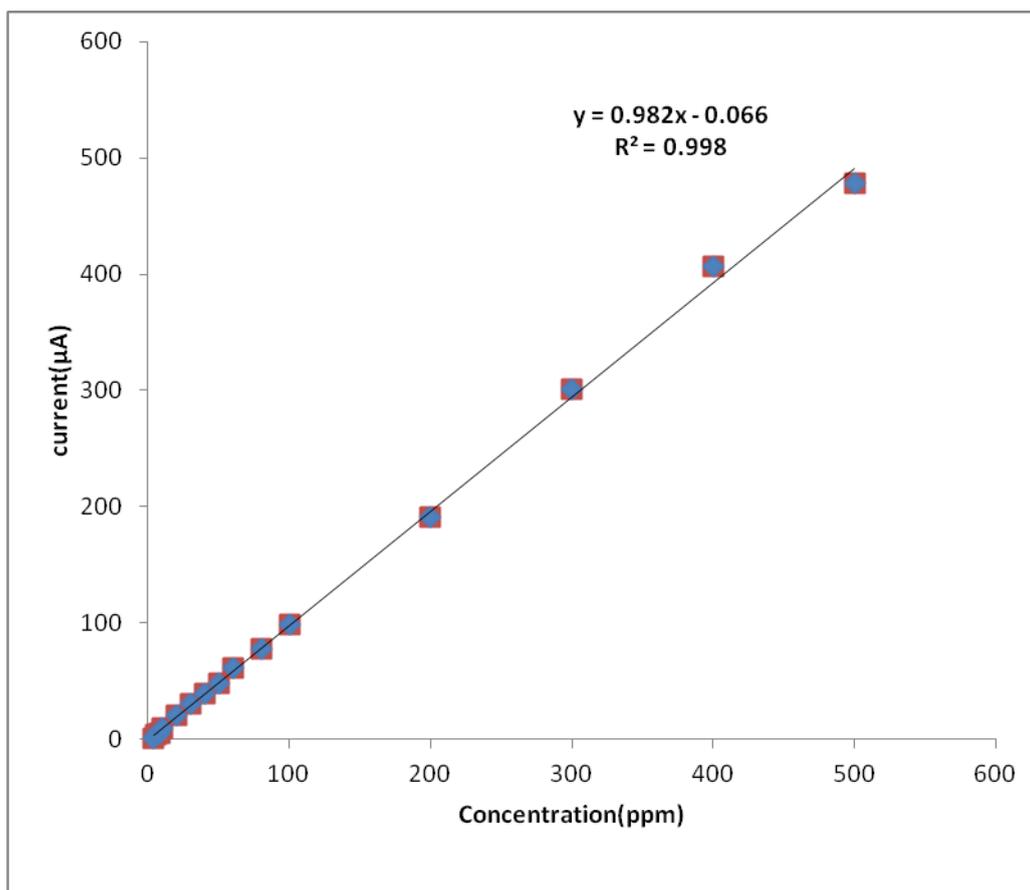
Figure 3. An extended calibration curve shows the relationship between Fe(II) concentration and the anodic peak current measured from the voltammograms for Fe(II) in 0.50 M H_2SO_4 at iodine - coated platinum electrode. Scan rate = 100 mV/s.

The absence of the aforementioned voltammetric features is a manifestation of iodine adsorption at the surface of platinum electrode. The iodine-coated platinum is stable at a potential range from -0.25 to ~0.85 V. The potential was allowed to exceed 0.80 V only when deliberate removal of iodine from platinum surface and regeneration of the clean unmodified platinum electrode is desired.
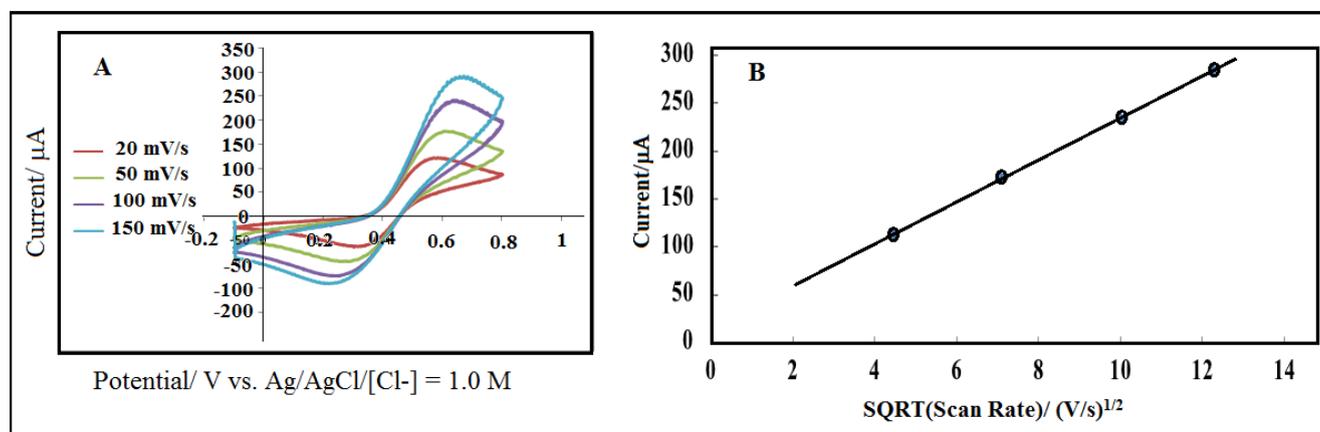
Figure 2 shows the cyclic voltammograms for the iodine-coated electrode recorded in a series of iron(II) standard solutions. The anodic peak currents were extracted from the voltammograms and plotted against the concentration of Fe(II) ions in the solutions to establish the calibration curve. The calibration curve for Fe(II) concentrations ranging between 4 and 500 ppm is displayed in Figure 3. The calibration curve shows a remarkable linearity (R^2= 9.995) and the calibration equation is given by

$$i\ (\mu A) = 1.023 C_{Fe(II)} + 2.903$$

Where i is the anodic peak current attributed to oxidation of Fe(II) to Fe(III). The counter cathodic peak which is assigned to reduction of the electrogenerated Fe(III) to Fe(II) shows a linear relationship between Fe(II) concentration but with a lower coefficient of determination, $R^2 = 0.94$ because of the higher uncertainty in assigning the level of the background current. For this reason, the anodic was taken as the analytical signal for Fe(II) determination.

Inter- and intraday calibrations were carried out to investigate the reproducibility of the developed method. The results indicate a very high similarity for the intra- and interday determinations where the coefficient of determination (R^2) is higher than 0.99 for both. The repeatability of the method was examined by reproducing the anodic current that is obtained for analysis of a 0.5 M H_2SO_4 solution that contained 50 ppm iron (II). The results indicated a coefficient of variation of 1.77% only which attests to the high precision of the developed method.

The effect of scan rate on the anodic peak current for oxidation of Fe(II) to Fe(III) at the iodine-coated electrode was investigated by reproducing the voltammograms for Fe(II) at different scan rates for scan rate values between 20 and 150 mV/s. Figure 4 indicates that there is a linear relationship between the anodic peak current and the square root of the scan rate, $(dE/dt)^{1/2}$ (R^2= 0.999) . This result is not unexpected for a diffusion controlled process. The deviation from linearity at higher scan rate values is expected and attributed to technical problems which arise with increasing scan rate. These problems are namely the increasing ohmic potential drop and the increasing charging current with increasing scan rate. For this reason, we have chosen 100 mV/s scan rate for determination of Fe(II) in aqueous solution.


Figure 4. A) Cyclic voltammograms of an iodine-coated platinum electrode in 0.50 M H2SO4 +200 ppm Fe(II) recorded at 20, 50, 100 and 150 mV/s. B) The least squares line for the anodic peak current vs. the square root of scan rate.

For determination of the linear concentration range, a set of Fe(II) solutions ranging from 4 ppm to 500 ppm Fe(II) were investigated. The results, as shown in Figure 3, indicate that an excellent linearity between the concentration and the anodic peak current for the range extending from 4 ppm to 500 ppm (R^2 = 0.996) is verified. This dynamic range which extends for more than two orders of magnitude is more than satisfactory for determination of iron concentration in dietary supplements and pharmaceutical preparations.

The limit of detection (LOD), (based on S/N=3) and the limit of quantitation (LOQ), (based on S/N=10) of the analytical method were calculated according to the standard procedures [14]. The values of LOD and LOQ are 2.34 and 7.8 ppm respectively.

3.2. Potential Interferences

Calcium, magnesium, zinc, selenium, copper, manganese, chromium, molybdenum, vanadium are common multimenerals that are usually contained in dietary supplements in addition to multivitamins some times.
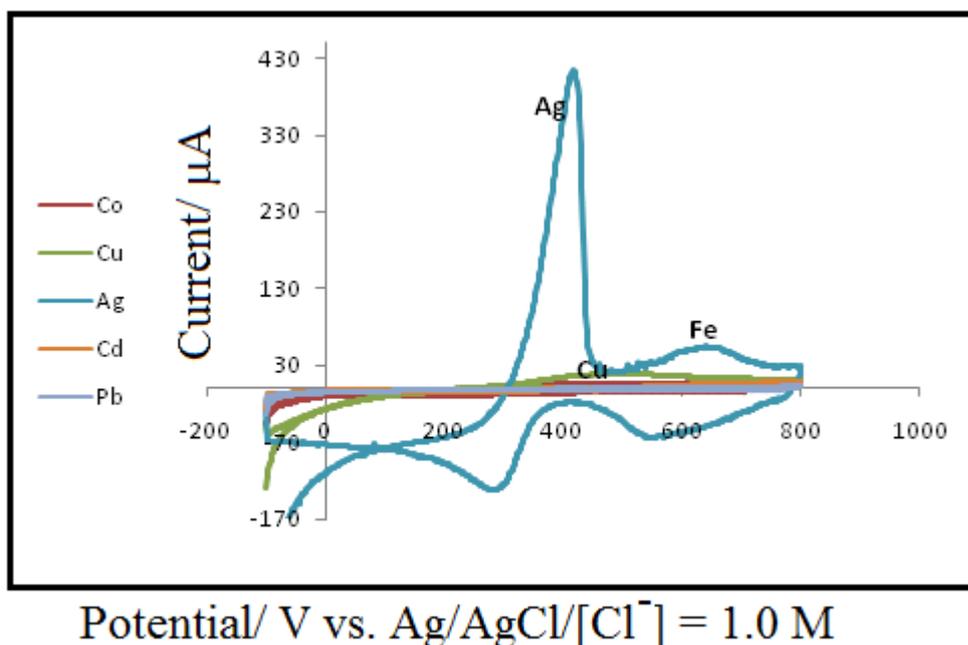
Figure 5. The voltammograms for an iodine-coated platinum electrode in 0.50 M H_2SO_4 containing 80 ppm Fe(II) in addition to 120 ppm of Co, Cu, Ag, Cd and Pb. Scan rate= 100 mv/sec. The legend on the figure indicates the color for each interferent.

The iodine-coated platinum electrode showed only a voltammetric response toward copper and silver and showed no response for the rest of the aforementioned ions (Figure 5). Silver, however, is not one of the essential elements to be added to dietary supplements. Iron anodic peak, on the other hand, is resolved from the broad copper peak as shown in Figure 5.

3.3 Analysis of real dietary supplement samples

Table 1 shows the results of voltammetric analysis of thee commercial dietary samples at an iodine-coated electrode. The data in Table 1 show that all the nominal values claimed by manufacturers are within the 95% confidence interval which indicates the absence of determinate or gross errors in the results. The values of the relative error for the three samples were all below 5% which attests to the accuracy of the developed method. The values of the coefficient of variation range from 0.74% to 2.7% which provides an unequivocal evidence for the precision of the developed method.

Table 1. Iron content in some dietary supplements collected from the Jordanian market as determined by linear sweep voltammetry at an iodine-coated electrode

Sample No.	Commercial Brand	Nominal mass (in mg) of iron/tablet or capsule	Average determined mass (in mg) of iron per tablet or capsule (mg) [1]	Standard deviation	95% Confidence limits	95% Confidence interval	Relative error	Coefficient of variation
1	Ferrous Gluconate®	35	36.69	±0.66	36.69±1.7	34.99 – 38.39	+4.8%	1.9%
2	Glucofer®	35	34.94	±0.26	34.94±0.65	34.29 – 35.59	-0.17%	0.74%
3	Fefol®	47	47 .50	±1.3	47.50±3.2	44.3 – 50.7	+1.1%	2.8%

[1]Average of three values

The paired t-test was applied to test for presence of a significant difference between the determined values of iron per tablet or capsule and the nominal values claimed by the manufacturers. The calculated t value is -0.68 while the critical t value is equal to 4.30 at p=0.05 (confidence level = 95%). This indicates that the null hypothesis is true and there is no significant difference between the determined values and the nominal values reported by the manufacturers at p=0.05.

In principle, iron can be determined by many techniques including UV/VIS spectrophotometry [15] AAS, ICP-AES, ICP-MS [14] differential pulse polarography [16] and ion chromatography[17]. Most of these methods are superior to the proposed method in terms of sensitivity. The sensitivity, however, is not a critical factor in analysis of dietary supplements because of the high concentration of iron the dietary supplements doses. The proposed method, however, is superior to all of these methods in terms of simplicity of instrumentation and absence of need for special or expensive reagents. The absence of complicated sample treatment is another added value to the developed method.

4. CONCLUSIONS

In the present work, the notion of using iodine-coated polycrystalline platinum electrode for determination of iron in dietary supplements has been verified. The developed analytical method is simple and requires no special reagents or sophisticated instrumentation.

The dynamic range for determination of iodine is between 8 ppm and 500 ppm Fe which is more than satisfactory for almost all practical purposes for analysis of dietary supplements samples. The absence of interference from presence of other metals is an added value to the method. Analysis of real samples collected from local drug stores and statistical analysis of the results indicated the absence of determinate errors and verification of the null theory that there is no significant difference between the results and the nominal values claimed by the manufacturers.

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