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Electrochemical Detection of ascorbic acid using Fe-Mn-SO4-2-/ZrO2(FMSZ) Modified Glassy Carbon Electrode

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Abstract A new ferric–manganese doped sulfated zirconia nanoparticle solid acid catalyst was prepared through the impregnation reaction followed by calcination at 600 oC for 3h and characterized by XRD, BET, EDS and TEM tools. The prepared electrode has been employed as a very sensitive electrochemical sensor through modification of glassy carbon electrode (GCE) with Fe-Mn- SO42-/ZrO2 (FMSZ). The electrochemical behavior of Ascorbic acid was studied by FMSZ/GC using cyclic voltammetry techniques. A well-defined oxidation peak was observed in 0.1 M KH2PO4 electrolyte solution by solid phase voltammetry. Under the CV techniques, it appears that the catalytic effect of the modification of FMSZ/GCE show higher current response as compared to bare GCE. Peak potential was observed to shift slightly to less positive value by about 220 mV and current was significantly enhanced by about 2.2 folds.

Keywords: Ascorbic acid,(FMSZ), nanocomposite, modified GC electrode, Cyclic Voltammetry.

الكشف الكهروكيميائي لحمض الأسكوربيك باستخدام (Fe-Mn-SO$_4^{-2}$ / ZrO$_2$FMSZ)كمادة على القطب الكربون الكهربائي الزجاجي المعدل

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الملخص تم تحضير محفز الحديدي المنغنيز بجزى النانو وعمل علية امتصاص وتم تحضير المحفز المنغنيز الحديدي الجديد من خلال تفاعل التشريب متبوعاً بالتكلس عند 600 درجة مئوية لمدة 3 ساعات ويتميز بأدوات XRD و BET و EDS و TEM. تم استخدام القطب المعد كمستشعر كهروكيميائي حساس للغاية من خلال تعديل قطب الكربون الزجاجي (GCE) مع Fe-Mn-SO42- / ZrO2 (FMSZ). تمت دراسة السلوك الكهروكيميائي لحمض الأسكوربيك بواسطة FMSZ / GC باستخدام تقنيات قياس الجهد الدوري. وقد لوحظت ارتفاع فى الأكسدة واضحة المعالم في محلول الإلكتروليت 0.1 م KH2PO4 بواسطة الفولتميتر الطور الصلب. وفقًا للتطبيق الطريقة الحهدية لوحظ أن التأثير الحفاز لتعديل FMSZ / GCE يُظهر استجابة حالية أعلى مقارنةً بالــ GCE العادية. وقد لوحظت ازاحة القمة اللاكسدة بتحول قليلاً إلى قيمة أقل إيجابية بحوالي 220 مللي فولت وتم ارداياد فى قيمة التيار بشكل ملحوظ بنحو 2.2 مرة.

الكلمات المفتاحية: حمض الالجبيك بالنانو، قطب الزجاج المعدل، حلقة الجهد الكهربي للأكسدة.

Introduction

The oxides of transition metal are considered as an important member of the family of inorganic compounds. They show many extraordinary physical properties, such as ferroelectric, magnetic, ionic conducting, superconducting and electrical conducting characteristics [1 -4]. In the meantime, these attractive metaloxides have a diversity of structures with fascinating phenomena.

Hence, transition metal oxides nanomaterial have been sightseen and applied in many technological filed. Recently mixed oxides of transition metals have been employed widely in industry assoiled catalysts since they can overcome many defects of the liquid ones. The strong acidity of the solid acid has attracted much attention owing to their capability to sa catalyze many operations, such esterification, cracking, alkylation, and isomerization .Moreover, zirconium oxide is an energetic enhancer designed for many chemical processes, in which its surface has different chemical features: reducing, oxidizing, acidic and basic. The activity of solid catalysts connected essentially with surface structures and strength of the dopants. The vitalfactorin optimizing surface features is the promoters 'choice. Furthermore, adsorption of different species, chiefly phosphate and sulfate anions, in transition metal oxides, is endeavored for improving the performance. Develop in the activity of the catalyst is expected to arise from growth of active sites of the modified transition metal oxides [5].Doping of different supports by sulfate anions could offer accessibility of active sites, thus, being more acidic compare to (100% H_2SO_4) and therefore classified as super acidic catalysts which are practical in the field of petrochemical industry[6].

The acidity of ferric–manganese promoted sulfated zirconium cannot be evaluated by the color-change indicators because of its shadowy color. Yet, it is considered as super acid, arbitrating from its catalytic performance for the isomerization of n-butane at ambient temperature [7]. The ferric–manganese promoted sulfated zirconia is indicated to be around three orders in level more active than sulfated zirconium for isomerization reaction[8-10] with large amount of super acid ssites, which shows that it has the highest acidity among solid super acids containing sulfate species. The analysis of ascorbic acid is important because it involves wide area of usage such as in drugs and as chelating agents for heavy metals in body. Ascorbic acid is essential in human body due to its importance in antioxidant property. Ascorbic acid is a water-soluble type of organic acid, which is also known widely as vitamin C. Many studies have been reported on the catalytic oxidation of ascorbic acid [17-22] .The key point of this research is the preparation of the Fe_2O_3-MnO-SO_4^{2-}/ZrO_2modified glassy carbon electrode and utilized for the analysis of ascorbic acid. The Fe_2O_3-MnO-SO_4^{2-}/$ZrO_2$was prepared via impregnation method and characterized by XRD, CV and SEM tools

2. Experimental

2.1. Instrumentation and electroanalytical analysis methods

Electrochemical workstations of Bioanalytical System Inc. USA: Model BAS 50W with potentiostat driven by electroanalytical measuring softwares were connected to the computer to perform cyclic voltammetry (CV). An Ag/AgCl (3M NaCl) electrode and platinum wire were used as a reference and counter electrodes respectively. The working electrode used in this study was a 3 mm diameter glassy carbon (GC). Unless otherwise stated, the voltammetric experiments were carried out at 25 ± 2oC using 0.1 M KH_2PO_4 as supporting electrolyte. Solutions were degassed with nitrogen for ten minutes prior to recording the voltammogram. Scanning electron microscopy (SEM) was used to characterize the surface of theFe_2O_3-MnO-SO_4^{2-}/ZrO_2 at 5 mm diameter basal plane paralytic graphite electrode (BPPGE)(Model JOEL,JSM-64000 machine).

2.2. Reagents

The pure commercial ZnO of ACS reagent was used, purchased from Fisher Scientific (Waltham, MA). Dimethyl sulfoxide (DMSO) was purchased from Ajax Finechem (Sydney, Australia) with 0.1% water content used as solvent. Deionized water was used in all the experiments. Deionized water from reverse osmosis (RO) water model Elken (BIO PURE) was used. Unless otherwise specified, the supporting electrolyte was 0.1 M KH_2PO_4 in aqueous media at room temperature. All solutions were deserted with oxygen-free nitrogen gas for 15 minutes prior to making the measurement.

2.3. Procedures

2.3.1 Preparation of FMSZ

5 grams of hydrate zirconium oxychloride $ZrOCl_2$ were dissolved in about 100 ml of deionized water, drop wise addition of 2.63 g of a 25% aqueous solution of ammonia led to precipitation. The precipitate was aging overnight, filtered by vacuum, washed several times until a negative test of chloride ion and dried for about 24 h at 393 K. $Fe(NO_3)_3·9H_2O$, $Mn(NO_3)_2·4H_2O$ and ammonium sulfate were dissolved in about 100 ml of distilled water in amounts corresponding to the desired stoichiometry and the solution was added drop wise under vigorous Stirring to zirconium oxyhydroxide solution and the mixture was left under vigorous stirring at room temperature for 4 h. The mixture is dried at 120 oC overnight calcined at 600 oC -3h.[2-6]

2.3.2. Preparation of (FMSZ) -modified glassy carbon electrode

A bare GCE was polished with alumina powder, rinsed ultrasonically with deionized water and dried at room temperature before use. Sample amounts of 0.1 mg of nanoparticles calcined at 600 oC for 3h. FMSZ were placed on a coarse grade filter paper. The glassy carbon electrode was pressed onto the substance and rubbed over the material, causing some compound to adhere to the electrode surface. The clean glassy carbon surface could be renewed after the measurement by polishing with 0.5 µm alumina slurry, followed by ultrasonic cleaning for about 2-3 minutes, rinsing with distilled water.

2.3.3 Characterization of Fe_2O_3-MnO-ZrO_2

The powder X-ray diffraction analysis was carried out using a Shimadzu diffractometer model XRD 6000. The diffract meter employing Cu-Kα radiation generated by Philips glass diffraction X-ray tube broad focus 2.7 kW type at ambient temperature. The crystallite size D of the samples was calculated using the Debye-Scherrer'srelationship[1].

$$Z = 0.9\,\lambda / (\beta \cos \theta) \qquad (1)$$

Where Z is the crystallite size, λ is the incident X-ray wavelength, β is the full width at half-maximum and θ is the diffraction angle.

The total surface area of the catalysts was obtained using Brunauer–Emmer–Teller (BET) method with nitrogen adsorption at −196 o C. Analysis was conducted using a Thermo Fisher Scientific (model: SURFER ANALYZER) nitrogen adsorption-desorption analyzer. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) was used to obtain information about the morphology and chemical composition of the samples. The morphological study of the catalysts was carried out using a JEOL scanning electron microscope model JSM-6400, while the quantitative chemical composition of the prepared Ferric- manganese promoted sulfated Zirconium acid catalyst was characterized using energy dispersive X-ray spectroscopy (EDS) for elemental chemical analysis.

3. Results and Discussion

3.1. Powder X-ray diffraction

The XRD patterns of support zirconia,Figure1, reveals a well crystallized monoclinic phase with a few amount of tetragonal phases. The monoclinic phase diffraction lines were appearing at (2θ =17.5 ,24.1 ,28.2 ,31.5 ,34.4 ,35.4, 38.6, 40.7, 44.8, 45.5, 49.3, 54.1, 55.7, 57.2, 62.8, 65.7o) (JSPDS file No: 00-007-0343 ZrO2)and that for tetragonal phase lines located at 2θ= 50.1 and 60.2o (JSPDS file No: 00-014-0534 – Zirconium oxide).While the patterns for Fe-Mn-promoted sulfated Zirconium (FMSZ) catalyst consists of only tetragonal ZrO2 phase located at 2θ = 30.2,34.7,50.1,60.2o (JSPDS file No: 00-014-0534 – Zirconium oxide). The peak corresponding to the monoclinic phase was absent in the Iron-manganese promoted sulfated zirconium XRD patterns signifying the stabilization of the tetragonal phase. The absence of characteristic peaks matching to Fe2O3 and MnO imply that the metal oxides are present in the form of solid solution or it is well dispersed on the zirconium surface. The dispersion of Fe2O3 and MnO particles causes the stabilization of the tetragonal phase and also imparts higher surface area.

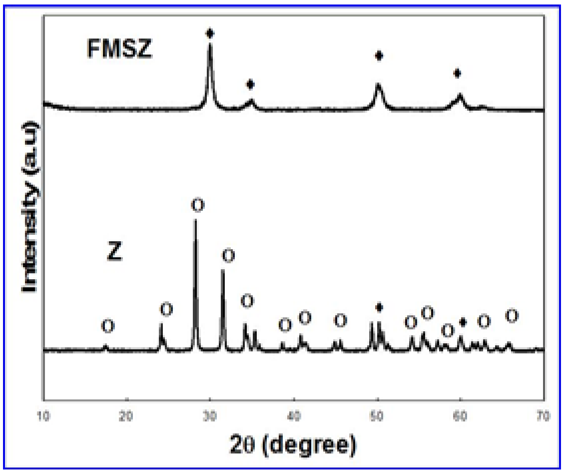

Fig 1. Monoclinic phase; (♦) tetragonal phase.1 XRD patterns of FMSZ (Fe-Mn-SO4/ZrO2) and Z (ZrO2) catalysts calcined at 600 oC for 3h.

To identify the effect of sulfate content on the iron-manganese-promoted sulfated zirconium quantitatively, the crystallite sizes of zirconium and FMSZ were obtained from the broadening of the strongest peak of the samples and based on Debye-Scherrer equation. The addition of sulfate was associated with a reduction in crystallite size to become 25.5, 14., nm for zirconium (Z) and FMSZ, respectively as depicted in table 1. This may be attributed to the sulfate groups that remain bounded at the surface of the catalyst and inhibit the growth of zirconium crystallites, in agreement thus with the other transition metal oxides. The decrease in the crystallite size can be explained by the hypothesis that the dispersed Fe2O3 and MnO particles along with bulky sulfate species on the surface of zirconium particles prevent their agglomeration during calcination.

Table 1.Influence of sulfate loading on the surface area, pore volume and crystallite size of FMSZ (Fe-Mn-SO4/ZrO2) and Z (ZrO2)

Sample	BET (m2g-1)	volume of pore (cm3g-1)	size of crystallite (nm)
ZrO236.0	0.00055	26.0	25.5
FMSZ	74.0	0.01888	14.5

The Specific surface areas and average pore sizes for the studied catalysts obtained using BET method, was 74, 36,0 m2/g, 40 nm , respectively as depicted in Table 1. It was also observed that the incorporation of Fe-Mn dopants and sulfate group in the structure of zirconium caused an increase in specific surface area and pore size of iron-manganese promoted sulfated zirconium. Jacobson reported that, the pore structure was a primary requirement for an ideal solid catalyst for biodiesel production since a typical triglyceride molecule has a pore diameter of approximately 58 ˚A (5.8 nm)[11-16].Since the average pore size of the catalyst was 40.0 nm, which was large, reactant can easily diffuse into the interior of the catalyst powder. This allowed reactants to be in contact with more acid sites, and the catalyst would have better activity.

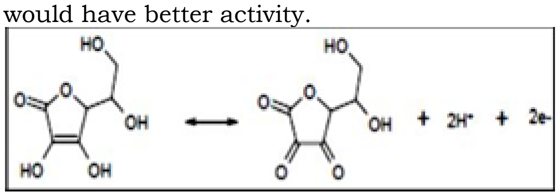

Fig.1. Ascorbicacid structure

.3.2Enhancement Study

The cyclic voltammograms of 0.1mM AA in 0.1M KH2PO4 aqueous electrolyte solution were obtained with a potential scanning at a positive direction over the potential range of -200mV to +800mV at a scan rate of 100mV/s for modified and bare GC electrode versus Ag/AgCl (Figure 3). Voltammograms recorded for all the electrodes appear to be irreversible.

AA oxidation current enhancement was detected when using GC and FMSZ/GC modified electrode; enhancement factor is 2.2 respectively. However, it was noted that the peak potential shifted negatively towards the origin by about 86mV when using the FMSZ /GC modified electrode indicating that slightly lower activation energy is required for the oxidation process. The slight shift observed in the over potential and the enhancement of the oxidation current signifies that the FMSZ /GC modified GC electrode possess a good electrocatalytic activity towards the AA oxidation.

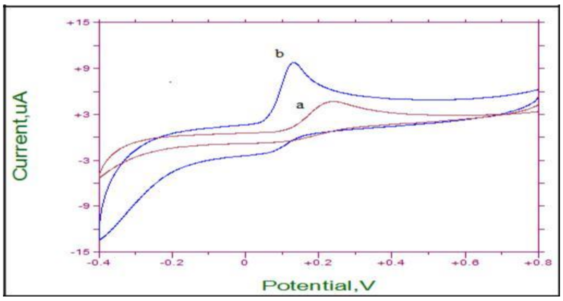

Fig. 3. Cyclic voltammograms for oxidation of 0.1 mM Ascorbic acid obtained in 0.1M KH2PO4 (pH 4.2), with potential scanning in the positive direction from -1000 to +1000 mV vs Ag/AgCl at a scan rate of 100mV/s at 25°C at (a) bare GC electrode and (b) modified FMSZ/GC.

the stability of the FMSZ/GC modified electrode and its effect on the oxidation current were assessed by continuous potential cycling over the potential range of oxidation current of Ascorbic acid . Figure 4 shows that the peak remained virtually constant throughout the 10 potential cycles, reflecting the stability of the FMSZ/GC modified GCE. This result can be related to the realization of steady condition in solid state cyclic voltammogram and the reaction is in equilibrium condition

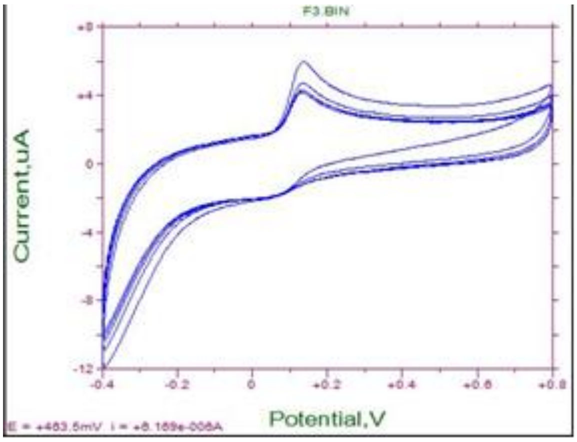

Fig. 4. Cyclic voltammograms pH for 0.1 mM Ascorbic acid l in 0.1 M KH2PO4with varying pH levels for GC electrode modified with modified FMSZ/GC modified GCE. Potential scanning in the positive direction from -400 to +800 mV vs Ag/AgCl at a scan rate of 100mV/s

3.4. Effect of varying scan rate

The effect of varying scan rates on the cyclic voltammograms of 0.1 mM Ascorbic acid using FMSZ/GC modified working electrode in 0.1 M KH2PO4supporting electrolyte was studied over scan rate range of 5 –1000 mV/s. Oxidation currents were observed to increase with scan rate due to heterogeneous kinetics [Fig 5 (a)]. In the present experiment a linear relationship between log ip and log v1/2is obtained suggesting the diffusion of Ascorbic acid at surface of FMSZ/GCE [Fig 5 (b)], which can be expressed by the following equation:

$\log i_p = 0.47 \log v - 0.4339; R^2 = 0.9963$ (2)

A slope of 0.4681, which agrees with the theoretical slope of 0.5 for diffusion controlled process, was obtained.

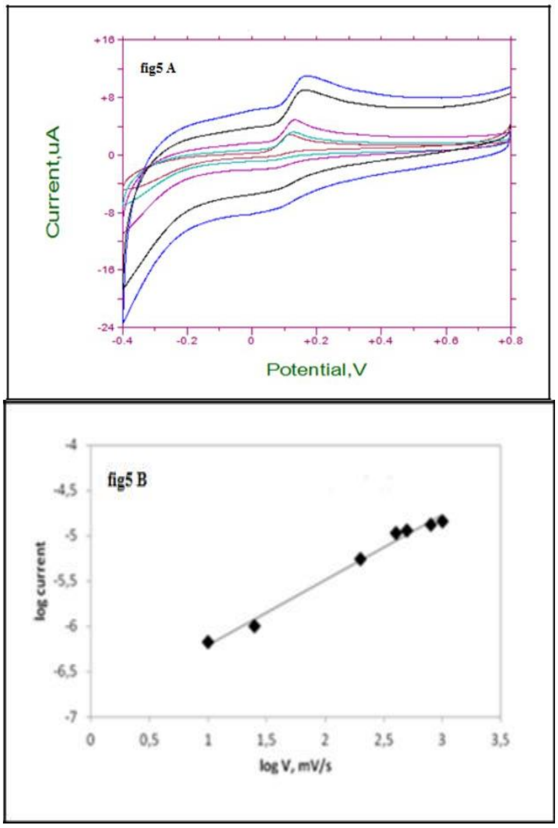

Fig.5.(A and B) Graph of log peak current versus log scan rate for0.1 mM Ascorbic acid l in0.1 M KH2PO4(pH 4.2), in different scan rate, for the FMSZ/GC modified GCE modified electrode with AA-Oxide modified electrode.

3.5. Effect of varying pH

The optimum working condition for AA oxidation at the FMSZ/GC modified GC electrode was determined by conducting a pH study on the supporting electrolyte solution. pH of the solution was varied from pH 3 to 8 in order to investigate its effect on the oxidation peak of AA. At both bare and modified electrode, it was observed that the oxidation current was high in the anionic condition up to pH 4.2, indicating the involvement of a proton transfer in the electrode process [18]. The pH continues to increase, a decreasing trend of the peak current starts to be seen for both bare and modified electrode (Figure 6). This may be contributed by the fact that AA is stable in basic solution [20-21]. And thus exist in anionic form and a repulsive electrostatic interaction occurs between the anions and the modified electrode surface [8] Since the maximum value of both oxidation current and enhancement factor (Figure 6) for the modified electrode was achieved at pH 4.2, therefore, the condition of supporting electrolyte at pH 4.2 was used for the rest of this study.

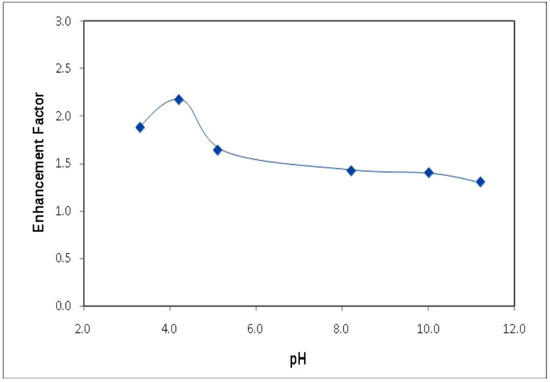

Fig. 6. Dependence of the oxidation current on pH using FMSZ/GC modified GC electrode in0.1 mM Ascorbic acid in 0.1 M KH2PO4 with potential scanning in the positive direction from -1000 to +800 mV vs Ag/AgCl at a scan rate of 100mV/s at 25°C and pH 4.2

3.6. Scanning electron microscopy (sem)

The morphology of the catalysts was studied by scanning electron microscopy (SEM). SEM images of zirconium and FMSZ were presented in Fig.7.In comparison with pure zirconium, SEM image of the FMSZ showed less agglomeration. This supports the retarding effect of metals and sulfate doping, on the development of crystallinity and prevention of agglomeration via sulfation enhancing stability of the tetragonal phase of zirconium and increasing surface area [7]. Spectrometer was used to analyze the percentage of elements present in the sample [17-20]. The quantitative percentage of iron-manganese promoted sulphated zirconium elements were found to be iron (Fe) – 0.60%,manganese (Mn) – 0.20%, sulphur (S) – 0.90%, zirconium (Zr) – 52.0% and oxygen (O) – 46.30%.

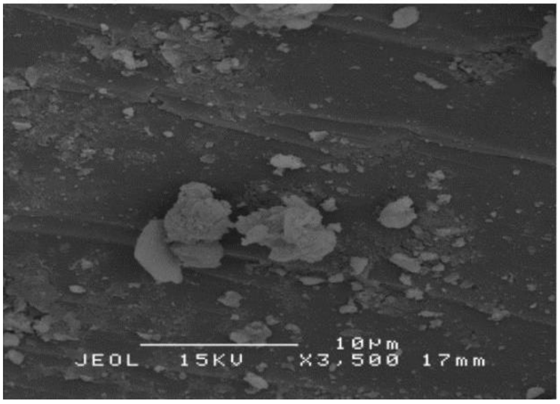

Fig. 7. SEM of Fe-Mn-promotedsulfated zirconia nanoparticles calcined at 600 °C for 3h

The image of the crystal presented in Figure 7, reveals a tetragonal shape of ferric-manganese-promoted sulfated zirconium. The particles in Figure 7 are uniformly distributed at the nanometer scale having a clear shape and different size, being approximately 50 nm with individual particles measuring 11–20 nm (without adding any organic surfactant) which matched very well with XRD data. The reproducibility of the method was established through the triplicate preparations and triplicate analyses.

4. Conclusion

Consistent with earlier reports, the iron–manganese promoted sulfated zirconium catalyst showed a higher surface area as compared to the zirconium sample. The dispersed Fe2O3 and MnO particles beside the sulfate group prevent the zirconium particles agglomeration leading to an enhanced surface area, acidity and hence its catalytic activity. The electrocatalytic behaviour of FMSZ/GC modified GC was studied by cyclic voltammograms. Conclusively, FMSZ can be used as an advanced carbon –based electrode matrix for the selective determination of Ascorbic acid. Upon modification with FMSZ, the oxidation peak current of Ascorbic acid was significantly improved due to high catalytic activity and conductivity of FMSZ/GC modified GC. Under the optimized conditions, the detection limit was found to be 4.869 x 10-8 M which is comparable to other electrodes and is of economic significance. Owing to the high sensitivity of FMSZ/GC modified GC, this method may be used for the detection of other compounds in food or biological fluids.

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