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An Optical ChemicaAl Sensor for Determination of Nickel in Water and Hydrogen Peroxide Samples

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Abstract

Application of nickel in different industries has been developed and so contamination of natural water is a great concern due to its potentially toxic effects on living beings. Therefore, fast monitoring of Ni^{2+} in aqueous samples is important. In this work, we fabricated a sensitive optical sensor for determination of nickel in mineral water samples and hydrogen peroxide solutions. The optode was prepared by incorporation of 1-(2-pyridylazo)-2-naphthol and sodium tetraphenylborate in a plasticized poly (vinyl chloride) membranes containing dioctyladipate as a plasticizer. The influence of several parameters such as pH, base matrix, solvent mediator and ligand concentration were optimized. Comparison the obtained results with previously reported sensors revealed that the proposed method, in addition to fast and simplicity, provided good linear range (1.70–85.20 μmol L^{-1}) and low detection limit (0.17 μmol L^{-1}). The precision (relative standard deviation) was better than 1.55% for 7 replicate determinations of 17.10 μmol L^{-1} of Ni in various membranes.

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Introduction

Nowadays, the pollution of natural water by heavy metals is a great concern due to their potentially toxic effects on living beings, therefore the detection and monitoring of toxic metals in water samples is necessary and very important [1].

Due to wide applications of nickel in different industries [2-6], its contamination of natural water leads to serious environmental hazards. Nickel and some its compounds can cause an allergic reaction, asthma, lung cancer and leukemia in human body originates [7-10]. Amount of nickel should not be more than 1.70 µmol L^{-1} in drinking water resources [11].

Hydrogen peroxide is used as a disinfectant, oxidizer and so forth in usual applications [12]. High concentration of hydrogen peroxide can be used either as a monopropellant or as an oxidizer for military applications [13]. If cationic impurities exist in commercial grade of hydrogen peroxide solutions, its purification to military grade (over 85%) can cause to explosion. So nickel concentration in commercial H_2O_2 solutions must be lower than 0.68 µmol L^{-1} [14]. Because of oxidation medium or presence of oxygen bubbles in H_2O_2 solutions, it is difficult to direct determining any ions before initial pretreatments. Therefore, it is important to develop a safe, selective and sensitive technique for the rapid measurement of Ni^{2+} in different media.

Determination of nickel is performed by several techniques such as x-ray absorption spectroscopy [15], flame and electro thermal atomic absorption spectrometry [16-20], atomic emission spectrometry [21], spectrophotometry [22, 23] and fluorescence spectroscopy [24]. Among the methods, spectrophotometric methods offer many appealing characteristics including: simple instrumentation, rapid response times and easy operation. These properties are desirable to the future design and development of portables analytical devices for nickel analysis.

Recently, an interest has been increased on the development of optical sensors compared to electrochemical sensors [25]. These sensors have better analytical characteristics [26] and they do not require internal and external reference devices, their time preconditioning are short and are not subjected to electrical noise [27]. The choice of the optode matrix is governed by the parameters such as permeability for analyte, cost, good mechanical properties and immobilization suitability for chromophore along with uptaking [28-30].

The most widely used polymers in optical sensors are poly (vinyl chloride) groups. They have many desirable features and compare well with sol–gel matrices for most applications [31]. Several optodes have been reported in trace analysis of different analytes such as metal ions, anions and organic compounds [32-37].

1-(2-pyridylazo)-2-naphthol) PAN) is a red solid which is readily soluble in common organic solvents such as methanol, ethanol etc. It forms coloured complexes with a large number of metal ions [38].

In this research, we introduced a selective, sensitive and rapid method based on PVC sensor for spectrophotometric determination of nickel by using PAN in water and hydrogen peroxide samples. According to the best of our knowledge, although analysis of Ni^{2+} was reported by this method previously but there is no information for monitoring of this cation in H_2O_2 media.

Experimental

Chemicals

All the chemicals were of analytical grade. 1-(2-pyridylazo)-2-naphthol)PAN), Low molecular weight poly vinyl chloride (LPVC, mol wt ~ 48000 g mol^{-1}), dioctyladipate (DOA) and sodium tetraphenylborate (NaTPB) were used without purification. Nickel solutions were prepared from a 17.04 mmol L^{-1} standard solution. A buffer of pH 6.0 was prepared from sodium hydroxide (0.046 M) and potassium hydrogenphthalate (0.05 M) solutions [39].

Apparatus

Absorption measurements were carried out on a Hitachi-U 3310 model Lambada-25 double beam UV-Vis spectrophotometer. The pH of the solutions was measured by a Metrohm model 691 pH/Ion Meter using a combined glass electrode.

Membrane preparation

The membrane consisted appropriate amounts of active components. 30.0 mg of PVC, 75.0 mg of DOA, 8.0 mg of PAN and 5.0 mg of NaTPB were transferred in a glass vial and dissolved into 1 ml THF. The solution was immediately shaken vigorously to achieve complete homogeneity. A glass plate (1×9×50 mm^3) was cleaned with pure THF and then placed in the spin-on device. Ninety micro liters of the above solution was injected to the glass plate. After 30 s spinning, at rotation frequency of 600 rpm, the membrane was located in ambient air and allowed to dry in air for few minutes.

Procedure

The sensing membrane (optode) was placed in a beaker filled with 20 ml of the test solutions containing EDTA (1.0×10^{-2} mol L^{-1}) and different concentration of Ni^{2+} (1.70 - 85.20 μmol L^{-1}) at pH 6.0. After 10 min the optode was mounted into the spectrophotometer directly and its net absorbance was recorded at 570 nm against a blank membrane.

Water samples (Mineral and river) were collected in 1 L amber glass bottles from Haraz (Anahita, Polur) and Jajrud (Lavasan) rivers in Iran. After sample pretreatments [34], 3 ml of each sample was spiked with appropriate amount of Ni (II) and was subjected to the above procedure.

Hydrogen peroxide (10-20%) samples were prepared freshly from commercial hydrogen peroxide (30%) solution after filtration. Then, each of samples after Ni (II) spiking was subjected to the membrane methodology.

Results and Discussion

Preliminary investigations

1-(2-pyridylazo)-2-naphthol)PAN) was recommended as a spectrophotometric reagent by Cheng and Bray where it gives a red dish colored chelates with metal ions as an example of Ni (II) [40]. Because PAN is organic, it is efficiently immobilized in the hydrophobic part of the membrane without prior lyophilization [41]. It was observed that by optimized fabricating a sensor from incorporation of PAN in a plasticized PVC membrane containing DOA, the determination of nickel could be practicable

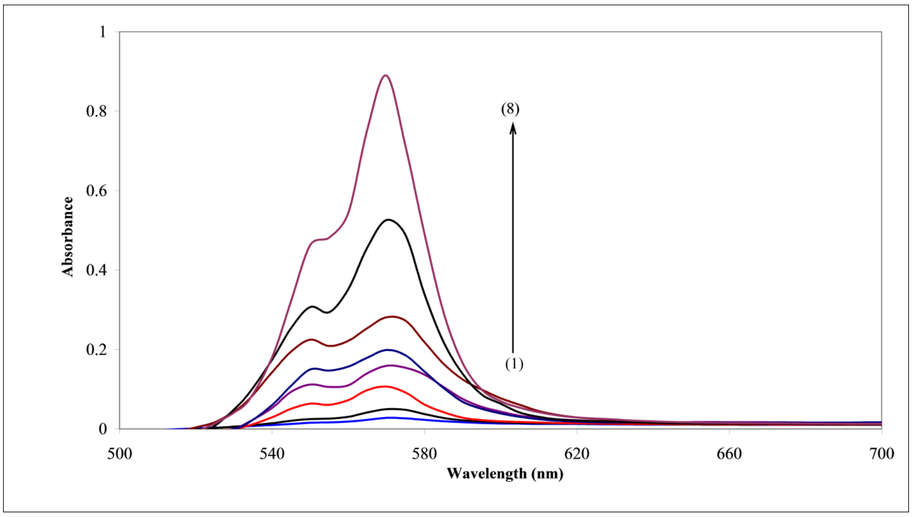

Figure 1. Absorption spectra of the proposed optode at various concentrations of Ni^{2+}: (1) 1.70, (2) 3.41, (3) 8.52, (4) 13.64, (5) 17.04, (6) 25.56, (7) 51.12, (8) 85.20 μmol L^{-1}; Conditions: pH=6.0; T=25°C; response time=10 min; membrane layer containing 25.42% PVC, 63.56% DOA, 6.78% PAN and 4.24% NaTPB.

spectrophotometrically.

When nickel ions diffused into the membrane, they formed a complex with PAN so the membrane colors changed from yellow to red. The absorption spectra of the PAN optodes in different concentrations of Ni (λ_{max}=570 nm) are shown in Figure 1.

Membrane composition

The response characteristics and working concentration range of each optical sensor depends significantly on the different ingredients such as base matrix, solvent mediator, ionophore and additive used in the membrane structure. Therefore the sensor matrix should be selected, firstly. In comparison of different polymers, low molecular weight PVC was observed as the best selection for the membrane base. This choice was due to several parameters such as appropriate transmittance, suitable immobilization of PAN without any leakage, good mechanical stability and reliable permeability to Ni^{2+} ions.

The nature of plasticizer is important and must be physically adaptable with polymer. In order to have a homogenous organic phase, several plasticizers such as dibutylphthalate (DBP), tributylphosphate (TBP), dioctylphthalate (DOP), ortho-nitrophenyloctyl ether (O-NPOE) and DOA were tested as potential plasticizers. From the graphs in Figure 2 (a and b), it was concluded that the membranes containing DBP, TBP, DOP and O-NPOE did not produced a suitable signals because of either improper physical properties with LPVC or leakage of PAN from the membrane. We found that DOA was the best selection with respect to good physical properties, the highest sensitivity and the lowest leakage.

As shown in Table 1 (membrane no. 1-5), the sensors with a weight ratio of DOA to LPVC as 2.5 provided best absorbance. Thus, 30 mg of PVC and 75 mg of DOA were selected as the optimum values. A decrease of the Ni^{2+} uptaking efficiency, at values lower than 75 mg, is explained by improper solidity of the optode that led to low diffusion of analyte cations into the membrane. At quantities more than 75 mg, flexibility of the optode increased, led to ionophore leakage into the test solution.

Effect of different amounts of PAN on the membrane response is observed in Table 1. As seen in membrane no. 6-10, the absorbance increased by increasing amounts of PAN up to 8 mg and decreased at higher amounts that were resulted from membrane leakages. Therefore, 8 mg PAN was selected as optimum value.

Due to the complete mass transfer of Ni^{2+} ions into the membrane and decreasing of response time, the presence of an anionic additive such as NaTPB facilitates the ion-exchange equilibrium [42]. The effect of NaTPB was investigated in the range 3.0-7.0 mg (membrane no. 11-15 of Table 1). It is shown that the highest absorbance is recorded by using 5.0 mg of NaTPB.

Effects of pH

The influence of media pH on the sensor response was studied in the range 4-8. As it is shown in Figure 3, optode absorbance increased at pH 6.0 and then decreased. At pH<6, protonation of the ligand prevents its reaction with Ni^{2+} ions and at pH>6.0, the response decreasing could be due to the hydrolysis of Ni^{2+} ions that is caused to incomplete diffusion of Ni^{2+} cations into the membrane. Therefore, a buffer with pH 6.0 was chosen in all experiments. In comparison, the optimum pH for Ni-PAN complex in aqueous solution has been reported as 6.5 [43].

Response time of optode

Response time of optodes is defined as the diffusion time of the metal ions from solution into the membrane (slowest step in complexation process) [44]. The effect of this parameter on the optode response was studied (Table 1 membrane no. 16-20). As seen, at least a time interval of 10 min is required for quantitative uptake at room temperature. It was observed that the optode response remained constant for more than 2 hours.

3. 5. Membrane properties

The properties of the optode membrane were measured by recording absorbance changed at 570 nm from individual solutions of 8.52, 17.04 and 51.12 μmol L^{-1} of Ni. As it is seen in Figure 4, in all of the three cases, the optodes reached to 98% absorbances after 10 minutes.

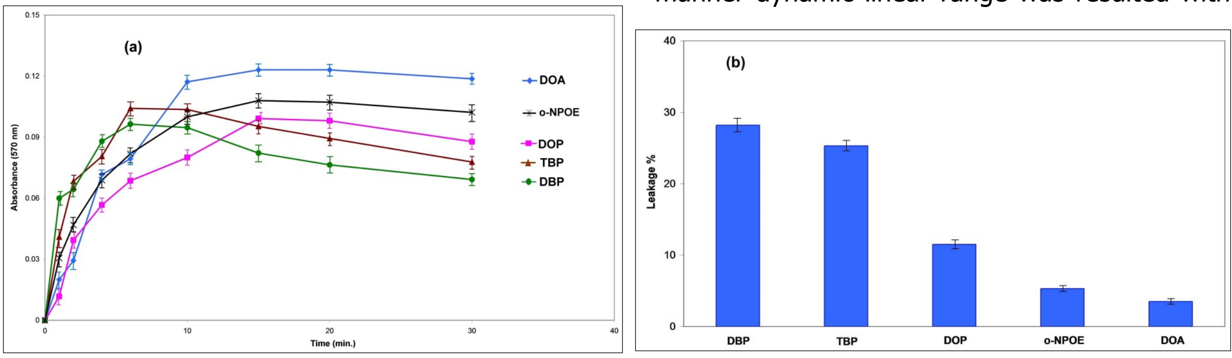

Figure 2. Effect of plasticizer nature on the response of the membrane after 10 min (a) and on the membrane leakage% after 30 min (b). Conditions: 34.08 μmol L^{-1} Ni^{2+}; T=25°C; membrane layer containing 30.0 mg of PVC, 75.0 mg of each plasticizers, 8.0 mg PAN.

The stability of membranes was tested for 2 hours and during this period a mean difference of absorbances for the mentioned solutions was ±0.007. Also the membrane responses were stable for one month in air.

The salting-out phenomenon on the optode response was investigated by adding different amounts of sodium nitrate. The results indicated that this parameter had no effect on the membrane response, up to 0.04 mol L^{-1} of $NaNO_3$ and above this concentration it was reduced slightly. This is due to a decrease in the activity of Ni^{2+} ions at higher concentration of electrolyte which reduces the interaction of nickel (II) cation with PAN in the membrane.

The sensor regeneration was studied by using of different compounds such as hydrochloric acid, nitric acid, sulfuric acid, sodium fluoride and oxalic acid in different concentrations. It was found that all of the reagents could not regenerate the optode membrane thoroughly and thus the membrane could be used as a probe (single test).

3. 6. Analytical characteristics

Table 2 summarizes the analytical characteristics of the optimized membrane. In this manner dynamic linear range was resulted within 1.70–85.20 μmol L^{-1} of nickel and detection limit was 0.17 μmol L^{-1}. Also the relative standard deviation (RSD %) for 7 replicate determinations of 17.10 μmol L^{-1} of Ni^{+2} in various membranes was 1.55% and so the method is reproducible during the experiments.

Table 3 presents a comparison between the proposed optode and the other sensors for determination of nickel previously [43, 45-48]. It is obvious that the obtained results of this work are comparable with these existing sensors. In some cases, it provides better linearity range and detection limit.

Table 2. Analytical characteristics of the proposed sensor.

Regression equation (n=12)	A = 0.1721C + 0.018, r = 0.9991
Linear range (μmol L^{-1})	1.70-85.20
Limit of detection (μmol L^{-1}) [a]	0.17
Reproducibility (RSD%) [b]	1.55

[a] For seven replicate determinations of the sensor in the absence of nickel (n=7).
[b] For seven replicate determinations of Ni: 17.10 μmol L^{-1}

Study of interferences

The selectivity of this sensor for determination of 8.52 μmol L^{-1} of Ni^{+2} was summarized in Table 4. The

Table 1. Effects of membrane composition on the absorbance of the proposed optode

Membrane	LPVC (mg)	DOA (mg)	PAN (mg)	NaTPB (mg)	Response time (min)	Absorbance (570 nm)a
1	30	65	8	5	10	0.197 ± 0.021
2	30	70	8	5	10	0.285 ± 0.012
3	30	75	8	5	10	0.357 ± 0.005
4	30	80	8	5	10	0.315 ± 0.009
5	30	85	8	5	10	0.177 ± 0.018
6	30	75	4	5	10	0.214 ± 0.017
7	30	75	6	5	10	0.303 ± 0.011
8	30	75	8	5	10	0.357 ± 0.005
9	30	75	10	5	10	0.348 ± 0.008
10	30	75	12	5	10	0.325 ± 0.010
11	30	75	8	3	10	0.231 ± 0.024
12	30	75	8	4	10	0.314 ± 0.011
13	30	75	8	5	10	0.358 ± 0.006
14	30	75	8	6	10	0.326 ± 0.017
15	30	75	8	7	10	0.280 ± 0.032
16	30	75	8	5	2	0.132 ± 0.023
17	30	75	8	5	6	0.300 ± 0.011
18	30	75	8	5	10	0.358 ± 0.004
19	30	75	8	5	12	0.359 ± 0.006
20	30	75	8	5	14	0.358 ± 0.005

[a] Mean absorbance ± SD (n=3) of each parameter is recorded from three solutions of 34.08 µmol L^{-1} Ni^{+2} (pH 6.0).

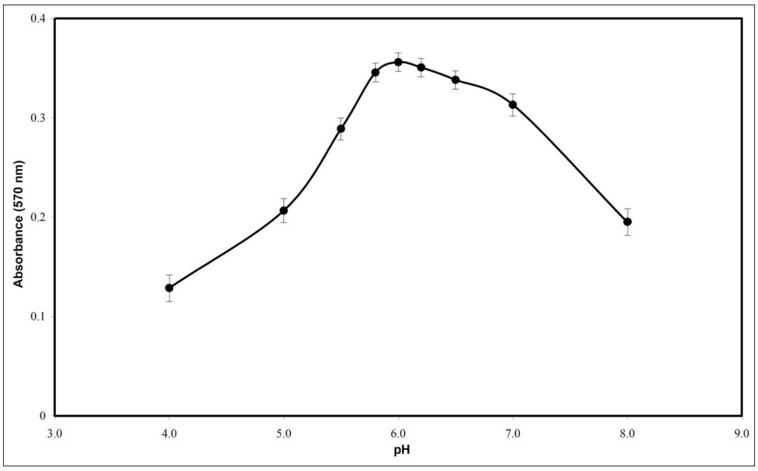

Figure 3. Effects of pH on the absorbance of the proposed optode; conditions: 34.08 µmol L^{-1} Ni^{2+}; T=25°C; response time=10 min; membrane layer containing 25.42% PVC, 63.56% DOA, 6.78% PAN and 4.24% NaTPB.

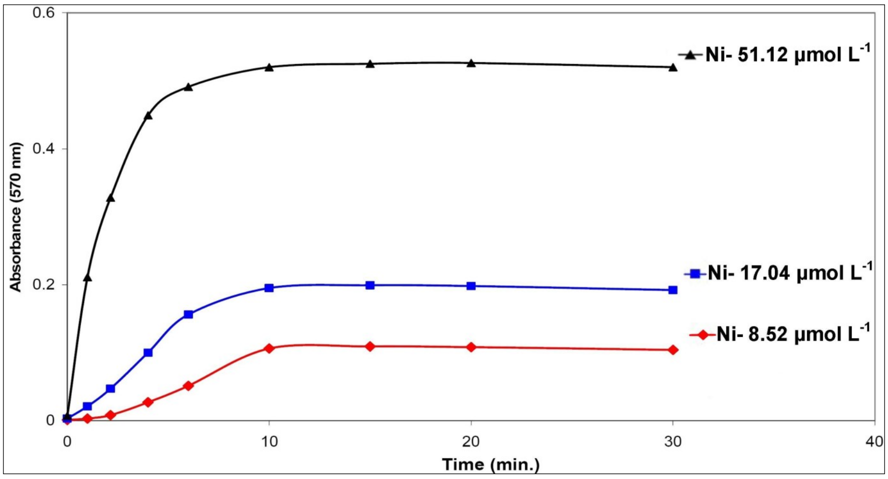

Figure 4. Response time of the optode membranes for different concentrations of nickel, Conditions: pH=6.0; T=25°C; membrane layer containing 25.42% PVC, 63.56% DOA, 6.78% PAN and 4.24% NaTPB.

Table 3. Comparison of optical sensor papers for Ni (II) determination

Membrane type	Ionophore	pH	LDR [a] (M)	LOD [b] (M)	Ref.
Nafion	1-(2-pyridylazo)-2- naphthol	6.5	2×10^{-5}-12×10^{-5}	1.7×10^{-5}	43
″	2-(5-bromo-2-pyridylazo)-5-(diethylamino) phenol	6.5	5. 1×10^{-6}-3.4×10^{-2}	8.5×10^{-6}	45
PVC	2-amino-1-cyclopentene-1-dithiocarboxylic acid	4-6.5	5.0×10^{-6} -1.0×10^{-3}	5.2×10^{-7}	46
″	1,2-di(*o-salicylaldiminophenylthio) ethane*	6	1.0×10^{-5}-5.0×10^{-3}	8.5×10^{-6}	47
Triacetyl cellulose -optical	triazene-1-oxide derivative	5.7	1.18×10^{-9}-7.34×10^{-5}	1.0×10^{-9}	48
PVC	1-(2-pyridylazo)-2- naphthol	6	1.70×10^{-6}-8.52×10^{-5}	1.70×10^{-7}	This work

[a] Linear Dynamic Range; [b] Limit of Detection

tolerance limit was defined as the concentration of added ion causing less than ±5 ٪relative error.

From Table 4, presence of alkaline metals and anions such as sulfate, chloride and others did not have adverse effects on nickel uptake. As seen, bivalent and some trivalent cations can interfere at different ratios. For elimination of these interferences, EDTA was selected as a masking agent. The effect of EDTA interfering was investigated firstly. It was resulted that $EDTA^{2-}$ did not affect (causing less than 4% negative deviation) on Ni measurement up to 1.0×10^{-2} mol L^{-1}. Thus, the presence of EDTA in the test solution can effectively mask 0.2 mmol of any interfering cations. Hence, the proposed membrane is a selective sensor for nickel monitoring in water and H_2O_2 samples.

3. 8. Method Application

The results of applicability of the membrane methodology are presented in Table 5. As shown, the mean recoveries for the addition of different concentrations of nickel to the water samples and H_2O_2 solutions were in the range of 98-104% and 98-105% respectively. Therefore, the proposed sensor can be successfully applied for the determination of nickel in the mentioned samples.

Conclusion

The proposed optode is a precise, low cost and sensitive device for determination of nickel, based on PVC membrane. Also the proposed method, in addition to fast and simple, provides a wide dynamic range, reliable reproducibility and a good limit of detection. EDTA was used as masking agent and the method could be made selective in this way. A comparison of the proposed optode with the previously reported sensors indicates that the proposed method in some cases provides wider linear range and lower detection limit. Finally, the fabricated sensor can be successfully applied to nickel monitoring in water and hydrogen peroxide samples. According to the best of our knowledge no manufactured optode has been reported in the literature for the determination of Ni in H_2O_2 solutions.

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Table 4. Tolerance limits of diverse ions on the Ni^{+2} (8.52 µmol L^{-1}) determination [a]

Foreign ions	Tolerance Ratio ($[M]:[Ni^{+2}]$)
Cations	
Na^+, K^+, Li^+ and NH_4^+	83.33403
Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+}, Cr^{3+}, UO_2^{2+} and ZrO_2^{2+}	4.167361
Mn^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+}, Zn^{2+}, Ga^{3+} and Cu^{2+}	2.084028
Co^{2+}, Cd^{2+} and Pb^{2+}	0.417361
Anions	
SO_4^{2-}, CO_3^{2-}, NO_3^-, NO_2^-, BO_3^- and HCO_3^-	83.33403
I^-, HPO_4^{2-} and PO_4^{3-}	41.66736
CN^-, Cl^- and F^-	0.834028

[a] ≤ 5.0% Deviation in the absence of masking agent.

Table 5. Determination of Ni^{2+} in different spiked samples

Samples [a]	Ni^{2+} (µmol L^{-1})		
	Added	Found [b]	Recovery (%)
Mineral	-	n.d. [c]	-
	1.7	1.77 ± 0.34	104
	13.63	13.46 ± 0.17	99
River	-	n.d. [c]	-
	6.82	6.64 ± 0.34	98
	17.04	17.38 ± 0.17	102
H_2O_2 (10%)	-	1.87 ± 0.51	-
	5.11	7.16 ± 0.34	103
	11.93	13.63 ± 0.17	99
H_2O_2 (20%)	-	2.90 ± 0.51	-
	3.41	6.47 ± 0.34	105
	13.63	16.19 ± 0.34	98

[a] Sample sources as described in the text.
[b] Mean value of three replicate determination ± Standard deviation.
[c] Not detected.

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