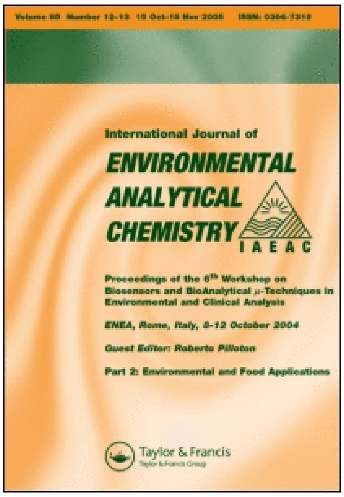

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Using 2,4 DNPH-PVC membrane sensors for indirect determination of formaldehyde in urea glue and wastewater

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Using 2,4 DNPH-PVC membrane sensors for indirect determination of formaldehyde in urea glue and wastewater

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Three simple, rapid, and sensitive ion-selective electrodes for indirect determination of free formaldehyde in urea glue and wastewater have been developed. The methods are based on the formation of the membrane sensors 2,4-dinitrophenylhydrazine-phosphtungestic acid (DNPH-PTA), 2,4-dinitrophenylhydrazine-phosphomolybdic acid (DNPH-PMA), and 2,4-dinitrophenylhydrazine-tetraphenylborate (DNPH-TPB) as neutral carriers. The sensors are stable and show fast potential responses of 30 s, and near-Nernstian cationic slopes of 56.2 ± 0.5, 54.3 ± 0.5, and 53.8 ± 0.4 mV per decade of activity between pH 0.5 and 3.5 over a wide range of 2,4-dinitrophenylhydrazine concentrations (1×10^{-5} to 1×10^{-2} M). These sensors were used for indirect determination of formaldehyde over concentration range (1×10^{-4} to 1×10^{-1} M). The selectivity coefficients of the developed sensors indicate excellent selectivity for 2,4 DNPH over a large number of organic and inorganic species. The mediator *o*-nitrophenyloctyl ether has a significant affect on the lifetime of the fabricated sensors. The analytical applications of the proposed sensors showed good results for indirect determination of formaldehyde in formaldehyde solutions, wastewater solutions, and free formaldehyde in urea-formaldehyde liquid and powder glues. The results were compared favourably with that obtained by ASTM, colorimetric, and British Standard methods.

Keywords: Formaldehyde; Potentiometry; PTA; DNPH; TPB; Sensors

1. Introduction

Formaldehyde is a possible human carcinogen and potential reproductive hazard. It enters the environment from construction products and is released by manufacturing facilities and combustion sources. It is also used in many industrial processes such as those of urea formaldehyde, melamine formaldehyde, phenolic formaldehyde, and sulfonated naphthalene formaldehyde resins, and because of its potential toxic effect, it is regarded as a principal indoor pollutant [1, 2]. Therefore, the need to develop simple and sensitive method for determining trace amounts of formaldehyde in wastewater or the free formaldehyde in its products has been a topic of ongoing concern [3].

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Numerous techniques are cited in the literature for determination of formaldehyde in air, including spectrophotometric analysis [4–15], chromatographic methods [16–22], electrochemical analysis [23–27], and chemiluminescence methods [28]. Recently, formaldehyde was determined in air using molecularly imprinted polymers [29] and hand-held photometers [30]. Biosensors based on enzyme/semiconductor nanoparticles or nanocluster systems [31, 32] and multiple-strain algal [33] and bi-layer biorecognition membranes [34] have been developed, but few articles have been published concerning the determination of formaldehyde in aqueous solutions by the ion-selective electrode technique [35].

In this work, efforts were made to prepare and characterize novel membrane sensors for indirect determination of formaldehyde in wastewater and free formaldehyde in urea glue. These sensors were based on the use of the ion-associate complex of 2,4-dinitrophenylhydrazine-phosphtungestic acid (DNPH-PTA), 2,4-dinitrophenylhydrazine-phosphomolybdic acid (DNPH-PMA), and 2,4-dinitrophenylhydrazine-tetraphenylborate (DNPH-TPB) as neutral carriers in a polyvinyl chloride (PVC) matrix membrane plasticized with *o*-nitrophenyloctyle ether. The proposed sensors have several significant advantages over many of the previously reported formaldehyde sensors and offer a lower limit of detection (1.9 $\mu g\,mL^{-1}$). These sensors cover a wide range of concentrations (1×10^{-4} to 1×10^{-1} M), display faster response times (20–30 s), and exhibit a reasonable selectivity in the presence of many common interfering ions. The sensors are satisfactorily used for determination of free formaldehyde in urea liquid and powder glues and in industrial wastewater.

2. Experimental

2.1 *Apparatus*

Potentiometric measurements were carried out at 25 ± 1°C with an Orion pH/mV metre Model 720 microprocessor ion-analyser. The three sensors based on 2,4-dinitrophenyl hydrazine-phosphotungestate, 2,4-dinitrophenylhydrazine-tetraphenylborate, and 2,4-dinitrophenylhydrazine-phosphomolybdate PVC membrane were prepared and used with an Orion double junction Ag/AgCl reference electrode (model 90-02) containing 10% (w/v) sodium nitrate solution in the outer compartment. The pH measurements were performed with an Orion (model 81-02) combination glass electrode. A Perkin-Elmer Lambada 15 UV/VIS spectrophotometer was used for absorbance measurements.

2.2 *Chemicals and materials*

All reagents were of analytical reagent grade unless stated otherwise. Doubly distilled water was used for the preparation of solutions of 2,4-dinitrophenylhydrazine hydrochloride (DNPH) and metal salts of different concentrations by diluting their stock standard solutions (0.1 M). Low-molecular-weight polyvinyl chloride (PVC), *o*-nitrophenyloctyl ether (*o*-NPOE), sodium tetraphenylborate (NaTPB), phosphotungestic acid (PTA), phosphomolybdic acid (PMA), and 2,4-dinitrophenylhydrazine (DNPH) were supplied from Sigma (St. Louis, MO). Tetrahydrofuran (THF) was obtained from Fluka. Formaldehyde solution (40%) and urea-formaldehyde liquid (60%) and powder glues were purchased from Sprea Misr Co. for Plastics and Chemicals (Ramadan City, Egypt). A standard stock solution (1×10^{-2} M) of 2,4-dinitrophenylhydrazine hydrochloride was prepared by dissolving 0.198 g of the 2,4-dinitrophenylhydrazine in 10 mL of conc. HCl and heated to 60°C until DNPH was completely dissolved, and then the solution was made up to 100 mL with double-distilled water. Dilute solutions of the DNPH (1×10^{-7} to 10^{-3} M) were freshly prepared from the stock solution and adjusted to pH 3 with 0.1 M sodium hydroxide.

2.3 *Preparation of ionophores*

The ion-association complexes (ionophores) 2,4-dinitrophenylhydrazine-phosphotungestic acid (DNPH-PTA), 2,4-dinitrophenylhydrazine-phosphomolybdic acid (DNPH-PMA), and 2,4-dinitrophenylhydrazine-tetraphenylborate (DNPH-TPB) were prepared by mixing 10 mL of 1×10^{-2} M of phosphotungestic acid, phosphomolybdic acid, or sodium tetraphenylborate with 10 mL of 10^{-2} M of 2,4-dinitrophenylhydrazine hydrochloride. The mixture was then shaken well, and the precipitates produced were filtered off through a Whatman filter paper (No. 42), washed with deionized water, dried at room temperature, and finally ground to a fine powder.

2.4 *Fabrication of PVC-DNPH membrane sensors*

A 10 mg aliquot of the complex ion associate (DNPH-TPA, DNPH-PMA, or DNPH-TPB) was mixed in a glass Petri dish (5 cm in diameter) with 190 mg of PVC powder and 360 mg of the plasticizer *o*-nitrophenyloctyl ether. The cocktail was dissolved in 5 mL of THF, and the Petri dish was covered with filter paper and left overnight to allow slow evaporation of the solvent at room temperature. A master PVC membrane (≈0.1 mm thick) was obtained, sectioned with a cork borer (10 mm diameter), and glued to polyethylene tubing as described previously [36, 37]. The electrodes were filled with a mixture of an equal volume of an aqueous solution (10^{-3} M) of 2,4-dinitrophenyl hydrazine hydrochloride and potassium chloride. The electrodes were pre-conditioned for 1 h by soaking them in 2,4-dinitrophenylhydrazine hydrochloride solution (10^{-3} M). A reference Ag/AgCl wire electrode (1 mm diameter) was immersed in the internal solution.

2.5 *Sensor calibrations*

The sensors were calibrated by transferring 10-mL aliquots of an aqueous solution (10^{-2} to 10^{-7} M) of 2,4 DNPH to 50-mL beakers followed by immersing the DNPH-PVC membrane sensors in conjunction with a double junction Ag/AgCl reference electrode in the test solution. The potential readings were recorded after stabilization to ±0.2 mV, and the e.m.f was plotted as a function of the logarithm of the 2,4 DNPH concentration. The calibration graphs were used for subsequent determination of unknown 2,4 DNPH concentration, and hence formaldehyde (FD) concentration was determined. The detection limit was taken at the point of intersection of the extrapolated linear segments of the calibration curve. The potentiometric selectivity

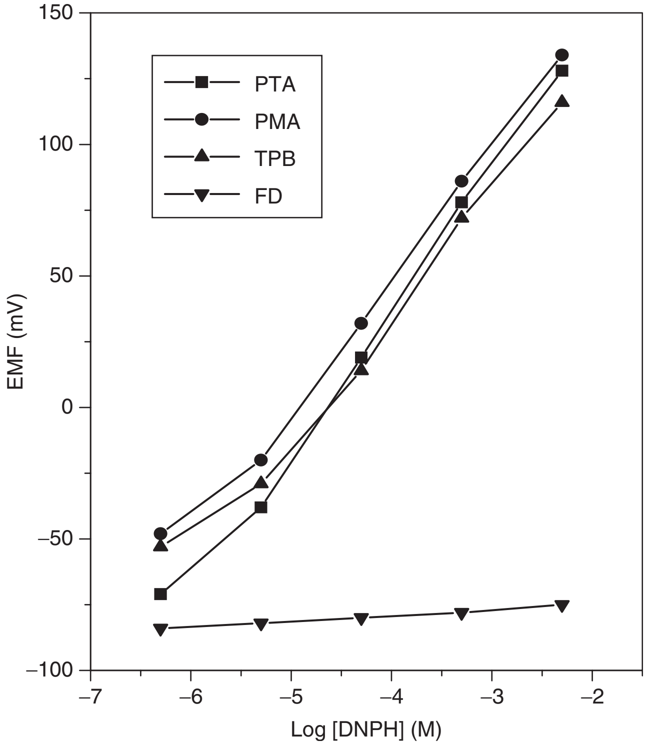

Figure 1. Potentiometric responses of DNPH using DNPH-PTA, DNPH-PMA, and DNPH-TPB PVC membrane sensors plasticized with *o*-NPOE at 20°C.

coefficients ($K^{pot.}{}_{DNPH,\ B}$) were also determined by the separate solution method (SSM) [32] using 10^{-3} M aqueous solutions of 2,4 DNPH and the interferents.

2.6 *Determination of formaldehyde*

2.6.1 Determination of formaldehyde in its solutions. Ten-millilitre formaldehyde solutions with concentrations ranging from 10^{-4} to 10^{-1} M were prepared and allowed to react separately with 20 mL of 10^{-2} M 2,4 DNPH after 5 min of constant stirring, and the unreacted 2,4 DNPH was determined from the calibration curve in figure 1. Then, the formaldehyde content was determined as follows:

$$[\mathrm{DNPH.HCl_{reacted\ with\ FD}}] = [\mathrm{DNPH.HCl_{total}}] - [\mathrm{DNPH.HCl_{unreacted}}] \tag{1}$$

Hence, the [FD] is determined from equation (2):

$$[\mathrm{FD}]\% = [\mathrm{DNPH.HCl_{reacted\ with\ FD}}] \times 0.0128. \tag{2}$$

2.6.2 Determination of free formaldehyde in urea formaldehyde liquid and powder glues. A 1-g aliquot of liquid urea formaldehyde glue of molar ratio 1 : 1.3 and from each type of four molar ratio of urea formaldehyde powder glue with different molar ratios of 1 : 1, 1 : 1.45, 1 : 1.6, and 1 : 1.8 (urea : formaldehyde) was suspended in 100 mL of distilled water, and then the mixture was stirred for 15 min. A 10-mL aliquot of the above solution was taken and added to 10 mL of 10^{-2} M of 2,4 DNPH and stirred for 5 min until a yellow precipitate of 2,4-dinitrophenlhydrazone was formed. The unreacted 2,4 DNPH was measured using 2,4 DNPH-PVC membrane sensors from the calibration curve in figure 1, and then the free formaldehyde was determined as mentioned above.

2.6.3 Determination of formaldehyde in wastewater from formaldehyde industrial plants. FD in wastewater was determined indirectly by collecting the wastewater from formaldehyde, 85% urea formaldehyde, urea formaldehyde liquid glue, and urea formaldehyde powder glue plants. A 100-mL aliquot of the wastewater was taken and filtered on G42 sintered gooch crucible, and then 20 mL of 10^{-3} M 2,4 DNPH was added. The mixture was then shaken well for 5 min until a yellow precipitate of 2,4-dinitrophenlhydrazone was formed. The unreacted 2,4 DNPH was measured using 2,4 DNPH-PVC membrane sensors, and then the free formaldehyde was determined as mentioned above.

3. Results and discussion

3.1 *Performance characteristics of the DNPH sensors*

The reaction of aldehydes and ketones with 2,4 DNPH to form 2,4-dinitrophenylhydrazone is well known and extensively used for determination of formaldehyde by spectrophotometric and HPLC techniques [16, 38]. Formaldehyde reacted with an excess of 2,4 DNPH to form a yellow precipitate of 2,4-dinitrophenylhydrazone up to 10^{-4} M of formaldehyde concentration, and the unreacted 2,4 DNPH was determined using the proposed sensors. Here, in this work, efforts were made to use the above reaction for determination of formaldehyde in wastewater and the free formaldehyde in urea liquid and powder glues using the ion-selective electrode technique in aqueous solutions. The method depends on the preparation of DNPH-PVC membrane sensors using DNPH-phosphotungestate, DNPH-phosphomolybdate, DNPH-tetraphenylborate, or ion associate complexes plasticized with *o*-nitrophenyloctyl ether. The sensors were used for determination of the unreacted 2,4 DNPH. The membranes were prepared using casting solutions of 28 : 2 : 70 wt% of poly (vinyl chloride), ion associate complex, and solvent mediator, respectively. Table 1 summarizes the response characteristics e.g. calibration slopes, response times, detection limits, and intervals of linearity over a period of 3 months for different assemblies of each sensor at the optimum pH and room temperature using IUPAC recommendations [39].

The sensors showed good behaviour regarding response time and reproducibility of e.m.f. values of the electrodes. Typical calibration graph and response characteristics of DNPH sensors based on DNPH-PTA, DNPH-PMA, and DNPH-TPB are shown in figure 1. At room temperature, the three sensors displayed linear response for 2,4 DNPH over the concentration range 5×10^{-5} to 5×10^{-1} M and calibration slopes of 56.2 ± 0.5, 54.3 ± 0.5, and 53.8 ± 0.4 mV per decade for DNPH-PTA, DNPH-PMA,

Table 1. Performance characteristics of DNPH- PVC membrane sensors plasticized with *o*-NPOE at 20°C.

	PVC membrane sensors		
Parameter[a]	DNPH-PTA	DNPH-PMA	DNPH-TPB
Slope (mV per decade)	56.2 ± 0.5	54.3 ± 0.5	53.8 ± 0.4
Intercept (mV)	225	215	207
Correlation coefficient (r) ($n = 5$)	0.997	0.998	0.997
Lower limit of linear range (M)	5×10^{-5}	5×10^{-5}	5×10^{-5}
Lower limit of detection (M)	1×10^{-6}	1×10^{-6}	8×10^{-5}
Response time for 1×10^{-3} M (s)	30	40	40
Working pH range	0.5–3.5	0.5–3.5	0.5–3.5

[a] Average of five measurements.

and DNPH-TPB sensors, respectively. The response time (t_{95}) of these sensors was tested by measuring the time required to achieve a 95% steady potential for 10^{-4} and 10^{-3} M 2,4 DNPH hydrochloride solutions when their concentrations were rapidly increased by one decade. Short response times of 30 s for $[\mathrm{DNPH}^+] > 10^{-4}$ M and 20 s for $[\mathrm{DNPH}^+] < 10^{-3}$ M were obtained. The sensors displayed constant potential readings within ± 1 mV from day to day, and the calibration slopes did not change by more than 0.5 mV per decade over a period of 3 weeks for PVC sensors. All the sensors exhibited constant slopes values during at least 6 weeks, followed by a gradual decrease in their sensitivity as time increased. The calibration graphs for the two electrodes were found to be reproducible from day to day provided that the sensors were stored in 10^{-3} M 2,4 DNPH hydrochloride solution before use.

3.2 *Effect of pH*

Measurements of the pH dependence of DNPH sensors were performed over a wide pH range (2–10). The pH was adjusted using dilute sodium hydroxide and/or hydrochloric acid. The potential–pH profile for 10^{-4} and 10^{-3} M DNPH solutions using the three sensors is summarized in figure 2a–c. The data revealed a linear potential *vs*. pH in the range of 0.5–3.5 from the point of view of sensor functions. It is apparent that, at $\mathrm{pH} < 0.5$, the DNPH sensors become progressively sensitive to the protonated DNPH species. In addition, the e.m.f. readings sharply decreased at $\mathrm{pH} > 4$ due to precipitation of the DNPH hydrochloride with gradual increasing concentration of unprotonated species.

3.3 *Effect of ions and cross-selectivity to aldehydes and ketones*

The potentiometric selectivity coefficient ($K^{\mathrm{pot.}}{}_{\mathrm{DNPH,B}}$) of the DNPH-PTA, DNPH-PMA, and DNPH-TPB PVC membrane-based sensors depends on the selectivity of the ion-exchange process at the membrane–sample interface, the mobility of the respective ions in the membrane, and the hydrophobic interactions between the primary ions and the organic membrane [40]. The selectivity of the DNPH membrane electrodes is also related to the free energy of transfer of the DNPH cation between the aqueous and the organic phases [41]. The potentiometric selectivity coefficients ($K^{\mathrm{pot.}}{}_{\mathrm{DNPH,B}}$) of the three sensors towards various ions were determined with 10^{-3} M aqueous solutions of DNPH

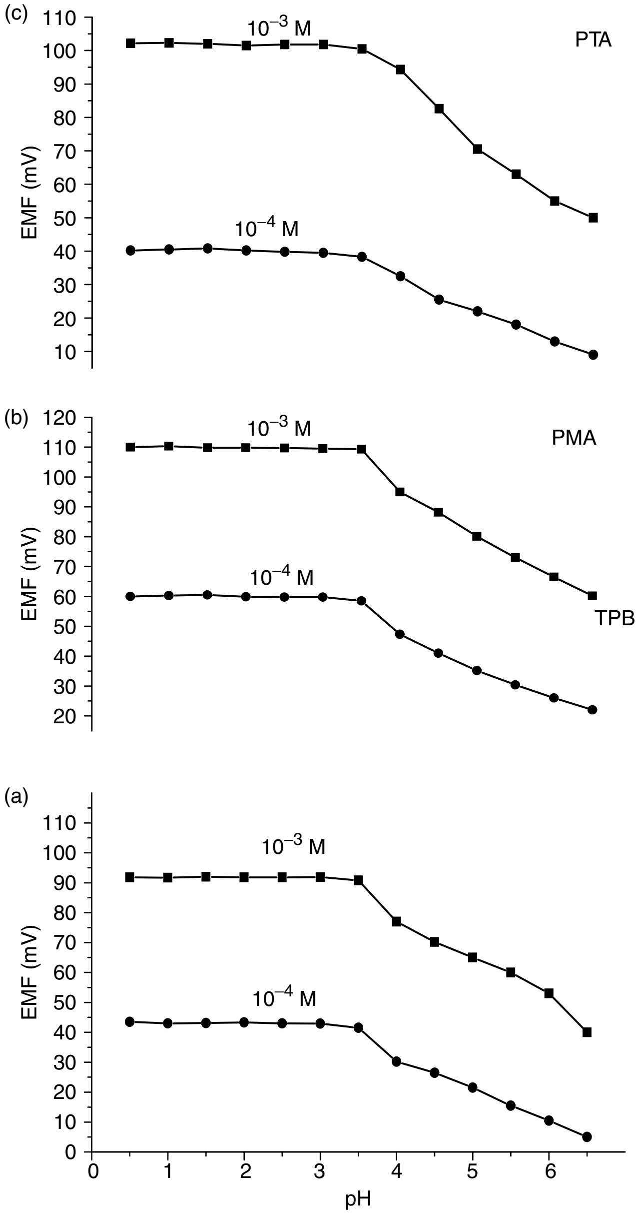

Figure 2. (a) Effect of pH on the potential responses of DNPH-TPB PVC membrane sensor plasticized with *o*-NPOE at 20°C. (b) Effect of pH on the potential responses DNPH-PMA PVC membrane sensor plasticized with *o*-NPOE at 20°C. (c) Effect of pH on the potential responses of DNPH-PTA PVC membrane sensor plasticized with *o*-NPOE at 20°C.

hydrochloride and the foreign compounds at pH 3 using the separate solution method employing the rearranged Niclosky equation [37, 39]:

$$\log K^{\text{pot.}}_{\text{DNPH}^{+},\text{B}} = \left[E^{+-}_{\text{DNPH}}\frac{E_{\text{B}}}{S}\right] + \left[1 + \frac{Z^{+}_{\text{DNPH}}}{\text{ZB}^{+}}\right]\log^{+}_{\text{DNPH}},$$

Table 2. Selectivity coefficient ($K_{\mathrm{DNPH,B}}{}^{\mathrm{Pot}}$) of DNPH PVC membrane sensors plasticized with *o*-NPOE.

Interferent, B	$K^{\mathrm{Pot.}}_{\mathrm{DNPH,B}}$ DNPH-PTA	$K^{\mathrm{Pot.}}_{\mathrm{DNPH,B}}$ DNPH-PMA	$K^{\mathrm{Pot.}}_{\mathrm{DNPH,B}}$ DNPH-TPB
$NH_4{}^+$	3.1×10^{-4}	5.8×10^{-4}	7.8×10^{-4}
Na^+	8.6×10^{-4}	1.3×10^{-3}	4.5×10^{-3}
K^+	1.0×10^{-4}	2.6×10^{-4}	5.6×10^{-4}
Mg^{2+}	5.2×10^{-4}	2.3×10^{-3}	5.1×10^{-3}
Ca^{2+}	1.2×10^{-2}	4.2×10^{-2}	7.3×10^{-2}
Cu^{2+}	2.1×10^{-3}	1.1×10^{-3}	4.2×10^{-3}
Co^{2+}	1.9×10^{-2}	1.3×10^{-2}	3.9×10^{-2}
Ni^{2+}	1.9×10^{-3}	1.1×10^{-2}	2.1×10^{-2}
Fe^{2+}	5.3×10^{-2}	1.1×10^{-2}	4.6×10^{-2}
Urea	1.3×10^{-3}	4.8×10^{-2}	9.2×10^{-2}
Thiourea	2.3×10^{-3}	3.2×10^{-3}	8.2×10^{-3}
Hydroxylamine hydrochloride	6.0×10^{-3}	7.4×10^{-3}	9.6×10^{-3}
Aniline	1.1×10^{-3}	3.2×10^{-3}	5.2×10^{-3}
Phenol	4.7×10^{-3}	1.3×10^{-2}	3.8×10^{-2}
Hydrazine sulphate	8.1×10^{-3}	1.1×10^{-2}	2.5×10^{-2}
Benzoguanamine	1.1×10^{-3}	2.5×10^{-2}	2.8×10^{-2}
Acetaldehyde	2.12	2.45	1.92
Acetone	1.98	1.75	1.82
Benzaldehyde	1.16	1.25	1.32
Methylisobutyl ketone (MIK)	1.01	1.12	1.15

where E_{DNPH} is the potential measured in 10^{-2} M for DNPH, E_{B} is the potential (measured in 10^{-2} M) of the interfering anion, $Z_{\mathrm{DNPH}}{}^+$ and Z_{B} are the charges of the DNPH and the interfering ions, respectively, and S is the slope of the electrode calibration curve plot. The results obtained are summarized in table 2. A good selectivity towards DNPH was achieved in the presence of many inorganic cations, such as Na^+, K^+, $NH_4{}^+$, Mg^{2+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, and Fe^{2+}, and organic compounds, such as amines, aniline, hydrazine sulfate, and phenols. However, there is essential interference from other aldehydes and ketones such as acetaldehyde, benzaldehyde, acetone, and methylisobutyl ketone (MIK), as shown in table 2, but the presence of these aldehydes and ketones in the samples under investigation is very rare. The interference from acetaldehyde and acetone was higher than from benzaldehyde and MIK which may be due to more miscibility with water. The sensor DNPH-PMA was found to be more selective than the DNPH-PTA and DNPH-TPB sensors.

3.4 *Analytical applications*

3.4.1 Potentiometric determination of formaldehyde in its solutions. The formaldehyde content was determined in its pure solutions by diluting 1.0 mL of FD solution (37–40%) to 100 mL with deionized water. Then, 5.0 mL of this solution was taken, mixed with 20 mL of 10^{-2} M of 2,4 DNPH, and shaken for 5 min until a yellow precipitate was formed. Next, the unreacted FD was determined by the proposed DNPH-PTA, DNPH-PMA, and DNPH-TPB sensors. The results are in good agreement with the expected values and compared favourably with the ASTM Standard method (table 3) [42]. The average recoveries of 99.6, 99.2, and 99.0%, with mean standard deviations of ±0.6, 0.7, and ±0.6%, obtained using the sensors

Table 3. Determination of formaldehyde in its solutions by DNPH-PTA, DNPH-PMA, and DNPH-TPB proposed sensors.

Formaldehyde solution samples	Mean formaldehyde recoveries (%)[a] ± SD			
	DNPH-PTA	DNPH-PMA	DNPH-TPB	ASTM Standard method[b]
Sample 1	37.3 ± 0.7	37.4 ± 0.6	37.2 ± 0.7	37.5 ± 0.5
Sample 2	38.5 ± 0.6	38.4 ± 0.8	38.1 ± 0.4	38.5 ± 0.7
Sample 3	37.9 ± 0.5	37.5 ± 0.7	37.7 ± 0.8	38.1 ± 0.8

[a] Average of five measurements.
[b] ASTM Standard method (sodium sulfite method).

Table 4. Determination of formaldehyde in wastewater solutions of different formaldehyde plants using the proposed sensors.

Sources of wastewater samples	FD found (%)[a] ± SD			
	DNPH-PTA	DNPH-PMA	DNPH-TPB	Colorimetric method[b]
Formaldehyde plant	0.0020 ± 0.7	0.0019 ± 0.9	0.0018 ± 1.2	0.0020 ± 0.7
Urea formaldehyde 85% plant	0.0035 ± 0.5	0.0036 ± 0.9	0.0035 ± 0.9	0.0035 ± 0.4
Urea formaldehyde liquid glue	0.0048 ± 0.8	0.0047 ± 0.6	0.0048 ± 0.7	0.0048 ± 0.7
Urea formaldehyde powder glue	0.0041 ± 0.4	0.0041 ± 0.6	0.0042 ± 0.8	0.0041 ± 0.7

[a] Average of five measurements.
[b] Standard colorimetric method [12].

DNPH-PTA, DNPH-PMA, and DNPH-TPB, respectively. The results in table 3 showed that the proposed sensors can be successfully used for selective determination of formaldehyde in its solutions.

3.4.2 Potentiometric determination of FD in wastewater solutions. The industrial wastewater from formaldehyde, urea formaldehyde 85%, urea formaldehyde liquid glue, and urea formaldehyde powder glue plants were collected. A 100-mL aliquot of the wastewater of each plant was taken and filtered on G42 sintered gush, and then 20 mL of 10^{-3} M 2,4 DNPH was added. The mixture was shaken for 5 min until a yellow precipitate of 2,4 dinitrophenlhydrazone was formed. The unreacted 2,4 DNPH was measured using 2,4 DNPH-PVC membrane sensors from calibration curve, and then the formaldehyde was determined as mentioned above. The results obtained (table 4) show that the formaldehyde (%) found in wastewater of FD, urea formaldehyde 85%, urea formaldehyde liquid glue, and urea formaldehyde powder glue plants are in good agreement with the data obtained by the colorimetric method [12].

3.4.3 Determination of free formaldehyde in urea formaldehyde liquid and powder glues. Five samples of urea formaldehyde glues with a molar ratio of 1 : 1.3 for liquid glue and 1 : 1, 1 : 1.45, 1 : 1.6, and 1 : 1.8 (urea : formaldehyde) for powder glues with free formaldehyde in the range of 0.3–0.5 for liquid glue and 0.1–0.3, 0.3–0.5, 1.0–2.0, and

Table 5. Analysis of free formaldehyde in urea formaldehyde liquid and powder glues.

	Mean recoveries of free formaldehyde (%)[a] ± SD			
Urea-FD glues	DNPH-PTA	DNPH-PMA	DNPH-TPB	British Standard method[b]
MR (1 : 1.3)	0.35 ± 0.8	0.37 ± 0.7	0.34 ± 0.9	0.36 ± 0.8
MR (1 : 1)	0.13 ± 0.9	0.12 ± 0.8	0.12 ± 0.7	0.13 ± 0.6
MR (1 : 1.45)	0.45 ± 1.1	0.43 ± 0.9	0.42 ± 0.8	0.45 ± 0.8
MR (1 : 1.6)	1.22 ± 0.7	1.23 ± 1.3	1.25 ± 1.2	1.25 ± 1.2
MR (1 : 1.8)	3.18 ± 1.2	3.24 ± 1.2	3.25 ± 1.1	3.2 ± 1.3

[a] Average of five measurements.
[b] British Standard method BS EN 1243 : 1999.

3.0–4.0% for powder glues, respectively, were prepared as mentioned in section 2.6.2 and used for determination of free formaldehyde. The results obtained (table 5) show an average recoveries of 98.14, 94.8, 96.9, 98.6 and 100.7% and mean standard deviations of ±0.8, ±0.8, ±0.9, ±1.0 and ±1.1% for 1 : 1.3, 1 : 1, 1 : 1.45, 1 : 1.6, and 1 : 1.8 (urea : formaldehyde), respectively. The results in table 5 showed that a good agreement was obtained with the results from the British Standard method [43]. Hence, the proposed method can be used for the determination of free formaldehyde in urea formaldehyde glues as an alternative method to the British Standard titrimetric method.

3.4.4 Comparison between the proposed sensors with other reported sensors. The comparison between the proposed sensors based on DNPH-PTA, DNPH-PMA, and DNPH-TPB and another previously reported sensor [35] showed that the proposed sensors are comparable and show a much better time of reaction for determination of formaldehyde with 2,4 DNPH (5 min), while the reaction of formaldehyde with Girard's reagent takes 1 h. Also, the response time was found after 1 min for the reported sensor where the proposed sensors responded after 30–40 s.

4. Conclusion

The prepared sensors DNPH-PTA, DNPH-PMA, and DNPH-TPB were used successfully for the analysis of formaldehyde content in formaldehyde solutions and in wastewater of formaldehyde and urea formaldehyde plants and free formaldehyde in urea glue liquid and powder at $>1.9\,\mu g\,mL^{-1}$. The developed sensors are selective, sensitive, and attractive in terms of their low cost and time saved in the routine control analysis compared with other reported sensors and more tedious spectrophotometric and titrimetric methods. The proposed sensors show favourable performance characteristics of pH, low detection limit, calibration slope, and a fast response. The sensors can be produced simply and reliably on a large scale and, for these reasons, may be regarded as being disposable.

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