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Synthesis of Fluorescence Chemosensor Pb^{2+} and Cu^{2+} Ions from Pyrazoline Derivatives Compounds with Lanthanum

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Abstract. Heavy metal ion pollutant waste Pb^{2+} and Cu^{2+} are getting attention due to the increasing amount, especially in various industrial field and transportation. The sensor of lanthanum (La) complexes with fluorescence-based pyrazoline derived has the potential to detect Pb^{2+} and Cu^{2+} heavy metal ions. The complex compounds were characterized by spectroscopic methode and stoichiometry of the La^{3+} pyrazoline complex was determined using the Job method. The determination of stoichiometric showed that 1 mole of lanthanum complex compounds can bind 10 moles of pyrazoline-derived ligands so that the predictable structure is bicapped square antiprism. The results of scanning the metal ion complex La^{3+} with pyrazoline-derived ligands using a UV-Vis spectrophotometer obtained three absorption peaks at 255 nm, 307 nm, and 359 nm with a molar absorptivity value (log ε) of respectively in 4.30; 4.25 and 4.13, three peaks are indicating the presence of a transition type $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. The results of the fluorescence spectrophotometer showed two emission peaks, the absorption peak of the La^{3+} complex compound was in the 370 nm region with fluorescence intensity of 2925 a.u and a 470 nm region with a fluorescence intensity of 796.4 a.u. The determination of the fluorescence chemosensor (fluorosensor) potential of the La^{3+} complex compound with the addition of Pb^{2+} and Cu^{2+} metal ions showed a significant fluorescence change so that the fluorosensor type was obtained for the La^{3+} metal ion complex compound with Pb^{2+} and Cu^{2+}, namely "turn-on" and "turn-off" respectively.

Keywords : Chemosensor, Fluorescence, Lanthanum, Pyrazoline

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Introduction

The exposure of lead (Pb) and copper (Cu) heavy metal ions in Indonesia to humans and the environment has received increasing attention over the last few decades as a result of the increasing application of heavy metals in various industries and transportation. Fluorescence-based sensors have been widely used in various fields, such as biomedical biochemistry and clinical studies, as well as environmental pollution problems such as the detection of heavy metals Pb^{2+} and Cu^{2+} [1]. This is because fluorescence-based sensor applications have the advantages of high sensitivity and selectivity, low cost, and fast detection [2]. Hakim (2016) succeeded in synthesizing the pyrazole derivative 2-(1,5-diphenyl-4,5-dihydro-1H-pyrazole-3-yl)pyridine with the addition of metal ions La^{3+} to form a complex organic ligand that acts as a turn-type fluorosensor on-off [3]. According to research by Zulys and Rachmawati (2017), the Eu^{3+} complex synthesized for Pb^{2+} and Cd^{2+} ion fluoresensors showed that the addition of Pb^{2+} and Cd^{2+} metal ions acted as turn -on and turn-off types of fluorosensors. The complex compound used can be used as a fluorosensor if the compound is an aromatic compound, heterocyclic or conjugated molecule [4]. Complex compounds can be formed because some metals and ligands form coordination covalent bonds [5].

The ligand para-di-2-(1-phenyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl)benzene is a derivative of pyrazoline which is a five-membered heterocyclic ring compound and contains two nitrogen atoms which act as as a free electron donor that can coordinate and chelate the central metal ion, namely La^{3+}, causing the formation of light absorption and emission and strong fluorescence properties. This is because lanthanum metal ions have a high affinity for pyrazoline-derived ligands as N-donors, so ligands with pyrazoline rings can affect the photo-physical properties of lanthanum metal ions [5,6,7]. Based on the background described above, this study aims to synthesize a complex compound from the metal ion La^{3+} with a pyrazoline derivative ligand, namely para-di-2-(1-phenyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl) benzene and its potential as a fluorescence-based Pb^{2+} and Cu^{2+} heavy metal sensor, because to the author's knowledge no one has researched this.

Experimental

This research was initiated by the synthesis of a complex compound from metal $La(NO_3)3.6H_2O$ with pyrazoline derivatives ligand is following procedure that previously reported [8,9]. The results of the synthesis of complex compounds were tested for their potential as fluorosensors against heavy metal ions Pb^{2+} and Cu^{2+} using a spectrofluorometer.

A total of 1 mmol of pre-synthesized ligand and 1 mmol of $La(NO_3)_3$ were dissolved in 20 ml of methanol p.a in different beakers. Next, the two solutions were mixed and stirred using a magnetic stirrer for 35 minutes at room temperature and pressure. The resulting solution and precipitate are yellowish-brown in color. After the precipitate was obtained, it was filtered and washed using cold methanol and cold hexane and then allowed to stand in a desiccator. The resulting complexes were characterized by fourier transform infrared spectrophotometer (FTIR), UV-Vis spectrophotometer, Melting Point Apparatus and fluorescence spectrophotometer.

The stoichiometry of ligands and metals was carried out by the Job method, the ligands and metals were dissolved in a methanol and chloroform solvent (1:1) respectively in a 100 ml measuring flask until the concentration became $5x10^{-5}$ M. Comparison of moles of ligands and metals showed the formation of coordination compounds. The addition of a ligand solution to the La(III) metal solution is diluted with methanol and chloroform solvents (1:1) in a 20 ml measuring flask. Then absorbance measurements were carried out with a UV-Vis spectrophotometer at the maximum wavelength. Then a comparison graph was made between the ligand mole and the metal mole La(III) on absorbance so that the intersection of the straight line formed was obtained which was a comparison of the stoichiometry of complex compounds.

Fluorescence experiments begin with measurement of the fluorescence intensity of complex solutions with the addition of metal ions Pb^{2+} and Cu^{2+} was used to determine the optimum concentrations of metals Pb^{2+} and Cu^{2+} which can cause a enhanced or quenced in the maximum fluorescence intensity. The complex compound at a concentration of $5x10^{-5}$ M was dissolved in methanol and chloroform (1:1), then metal ions Pb^{2+} and Cu^{2+} were added in the concentration range from $5x10^{-4}$ M to $5x10^{-7}$ M. Next was scanned at a wavelength of

220-550 nm. The results obtained were plots of emission and excitation intensity with respect to wavelength. This measurement was used to determine the selectivity of complex compounds on the addition of heavy metal ions Pb^{2+} and Cu^{2+}.

Result and Discussion

The metal ion complex compound La^{3+} with the ligand is obtained which is yellow, and the melting point is 268.8° C. If the melting point of the complex compound is higher than the melting point of the ligand, this indicates that the complex has been formed. This can be proven from the experimental results that the melting point of the ligands is 230.9°C and the melting point of complex compounds is 268.8°C. In the determination of stoichiometry (Figure 1), the central metal ions La^{3+} and ligands were measured at a maximum wavelength of 255 nm. The results of the analysis using the Job method showed that 1 mole of La(III) metal can bind to 10-11 moles of pyrazololine-derived ligands. In general, the La(III) complex has a coordination number of 5-11 with a varied complex structure, for the La(III) complex structure with a coordination number of 10 can be predicted to be a bicapped square antiprism structure [10].

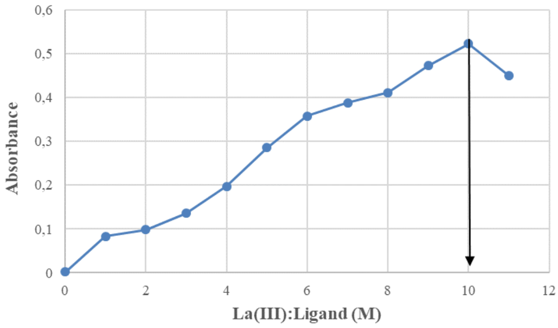

Figure 1. Stoichiometric graph of La^{3+} metals and pyrazoline-derived ligands

The synthesis of lanthanum complex compounds with pyrazoline derivatives ligands has La-N bonds (positive partial La and negative partial N) which has a difference in electronegativity of 1.94 (difference in electronegativity of lanthanum metal with element N) so that according to Pauling's theory, lanthanum complex compounds is a polar compound. In pyrazoline-derived ligands, the presence of conjugated electrons in the aromatic ring system of pyrazoline and pyridine ligands also affects the strength and stability of the ligands in forming a complex compound. This happens because the aromatic ring on the ligand has a bond whose electrons are delocalized. The delocalized electrons in the aromatic ring will increase the bond strength that occurs in the ligand and the central atom so that the more electrons are delocalized, the stronger the bond between the ligands and the central atom [11]. Based on the FTIR spectrum of the complex compound in Figure 2 and Table 1, wavenumber 3339.23 cm^{-1} indicates the presence of an amine bond [6].

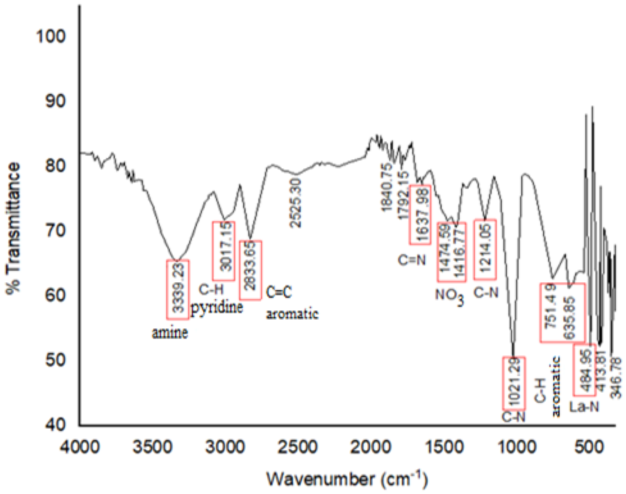

Figure 2. Spectrum FTIR La Complex Compound

The wavenumber of 3017.15 cm^{-1} is a C-H bond in the pyridine ring [3]. At a wavenumber of 2833.65 cm^{-1} is an aromatic C=C bond [12]. At wavenumber 1637.98, it is a C=N bond [13]. At a wavenumber of 1474.59-1416.77 cm^{-1} is an absorption band that is typical of the presence of nitrate ions (NO_3^-) attached to the La^{3+} complex compound [8]. At wavenumbers 1214.05-1021.29 cm^{-1} is a C-N bond [3,14]. At a wavenumber of 751.49-635.85 cm^{-1} is an out-of-plane bend aromatic C-H bond [14]. At a wavenumber of 484.95 cm^{-1}, it is a La-N bond [6].

The formation of complex compounds can be started by scanning the wavelength and then measuring the maximum wavelength with a range of 190-550 nm for complex compounds with La^{3+} ions, ligands and the metal ion La^{3+} shown in Figure 3. Two maximum wavelength peaks were obtained for the ligand in the region of 249 nm and 364 nm with a yellow solution, at a maximum wavelength of 249 nm, the absorption band of the aromatic chromophore group, namely the benzene group, occurs and at a wavelength of 364 nm, the absorption process occurs in the absorption band of the ligand

Table 1. Results of wavenumber shift of ligands and La complex compounds

Bond	Wavenumber (cm^{-1})	
	Ligand	La^{3+} Complex
Amine	3332.17	3339.23
C-H pyridine aromatic	3009.08	3017.15
C=N	1649.21-1417.74	1637.98
C=C Aromatic	2830.66	2833.65
C-N	1218.10-1030.25	1214.05-1021.29
C-H Aromatic	754.20-665.47	751.49-635.85
NO_3^- ions	-	1474.59-1416.77
La-N	-	484.95

chromophore group, namely the pyridine group and the pyrazoline group. pyrazoline and pyridine are in the maximum wavelength range of 360-400 nm [15].

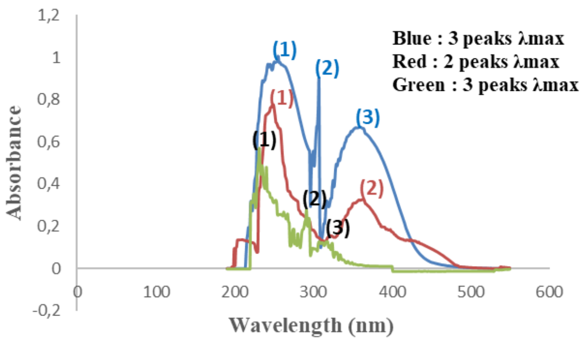

Figure 3. Maximum wavelength scanning results pyrazoline ligand solution (red), $La(NO_3)_3.6H_2O$ solution (green), La^{3+} complex compound solution (blue)

The maximum wavelength of $La(NO_3)_3.6H_2O$ solution was 231 nm, 291 nm, and 317 nm. At wavelengths of 231 and 291 nm is an indication of the absorption band process of metal ions La^{3+}[16] that the absorption of metallic La^{3+} is at a maximum wavelength of 238 and 301 nm then at a wavelength of 317 nm is an indication [17] that the absorption of nitrate ions is at a maximum wavelength of 313 nm. The results of UV-Visible analysis of complex compounds in Table 2 showed that there were three absorption peaks at the maximum wavelength of complex compounds, namely 255 nm, 307 nm, and 359 nm with a light yellow solution. The shift of peaks towards a larger wavelength is an early indication of the formation of complex compounds. In the spectra of the La^{3+} complex compound with pyrazoline-derived ligands, it has 3 significant absorption bands for the π – π* transition (C=C) in the 255 nm region, π – π* (C=N) in the 307 nm region, and the n – π* transition (free electrons on the N donor atom) in the 359 nm region. The maximum wavelength at the π – π* transition is lower when compared to the n - π* transition this is because the energy required for electrons to experience excitation from orbitals π to π* orbitals is higher than the energy required to excite electrons from non-n orbitals bonds to the π* orbitals [13].

In lanthanum nitrate hexahydrate, there is a charge balancing ion in the complex compound, namely the nitrate ion, so there will be interactions between the metal and the ligand which can change the energy gap between the free ligand orbitals and the color of the complex compound. This can also cause a shift in absorption toward shorter wavelengths (hypochromic) or towards longer wavelengths (bathochromic) [18]. The absence of significant absorption of the Ligand to Metal Charge Transfer (LMCT) absorption band estimated to be around 380–700 nm in the lanthanum(III) complex is due to the absence of 4f electron orbitals and the electron shielding effect of the rare earth 4f orbitals. Since the lanthanum(III) complex is one of the elements of the lanthanide series, no f-f transition absorption band can be observed because the f-f band is very weak [18,19]. The central metal lanthanide has a weak absorption coefficient so in the presence of a coordinated pyrazoline derivative ligand it will strengthen the high absorptivity coefficient and strong light absorption [20,21].

Table 2. UV-Visible absorption peak of La complex compounds

λ maks, nm (ε, $M^{-1}cm^{-1}$)	Absorbance	Log ε
255	1.008	4.30
307	0.892	4.25
359	0.671	4.13

The electron transition π–π* is characterized by relatively large molar absorptivity values (ε) and can be seen at 2 absorption peaks (255 and 307 nm), in addition to large molar absorptivity values indicating that this compound has a strong fluorescence intensity [13]. This analysis was carried out to observe the fluorescence characteristics of the metal ion complex La^{3+} with the ligand. The results obtained based on Figure 4 formed two emission peaks of complex compounds, namely in the 370 nm region with a fluorescence intensity of 2925 a.u and in the 470 nm region with an intensity of 796.4 a.u.

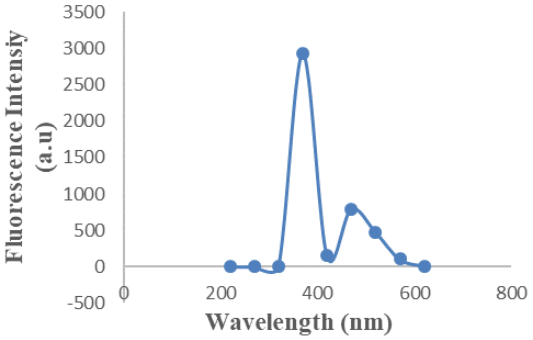

Figure 4. The Fluorescence Intensity Spectrum of La Complex Compound

The formation of two emission peaks in the metal ion complex compound La^{3+} is probably because when returning to the ground state, electrons first occupy a higher vibrational energy level found in the ground state before dropping to a lower level. A good probe has a high fluorescence intensity and a fairly wide stokes shift, this is to avoid interference in the detected environment if there are interfering compounds that can fluoresce [22].

The addition of heavy metal ions Pb^{2+} was carried out with several concentration variations ($5x10^{-4}$-$5x10^{-7}$ M) into the La^{3+} complex compound with a concentration of $5x10^{-5}$ M using methanol-chloroform (1:1). It can be seen in Figure 5 that there are 2 emission peaks when Pb^{2+} heavy metal ions are added at a wavelength of 370 nm and 470 nm, this is probably due to because upon returning to the ground state, electrons first occupy a higher vibrational energy level found in the ground state before dropping to a lower level, resulting in an increase in fluorescence in the 370 nm region and fluorescence quenching or cooling in the 470 nm region [22]. In compounds that can emit light, electrons from the π* state do not relax directly to the ground state but undergo intersystem crossing towards the triplet state of the central metal ion. The appearance of the emission peak of the lanthanum complex compound at 470 nm indicates that there has been an emission from the LMCT (Ligand to Metal Charge Transfer) event from the excited state of the ligand (S1) to the La^{3+} ion with the electronic transition π*. On the addition of heavy metal ions Pb^{2+} there was a shift in wavelength from 370 nm to 373 nm, this indicates an interaction between the La^{3+} complex compound and Pb^{2+} ions.

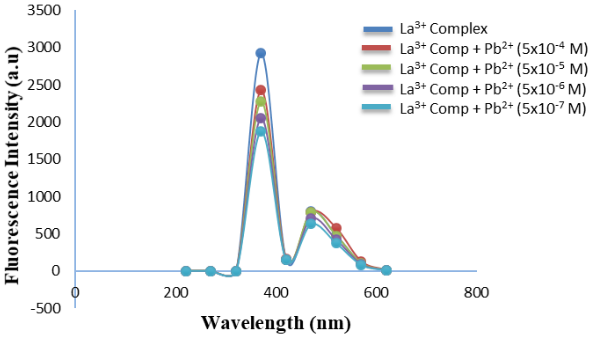

Figure 5. Fluorescence intensity spectrum of complex compounds on the addition of heavy metal ions Pb^{2+} at various concentrations

Research conducted by Zulys and Rachmawati (2017) obtained the maximum emission peak at a wavelength of 240 nm with fluorescence intensity of 285 a.u [4]. The research conducted by Hakim and Zulys (2016) obtained the maximum emission peak from pyrazoline-derived ligands with the addition of La^{3+} metal at a wavelength of 355 nm with fluorescence intensity of 341 a.u, while in the study of the La^{3+} complex compound with pyrazoline-derived ligands, the maximum emission peak was obtained at a wavelength of 370 nm with fluorescence intensity of 2925 a.u [3]. Then there was a shift in wavelength in the 373 nm region when the heavy metal ion Pb^{2+} was added possibly due to the addition of heavy metal ions Pb^{2+} with different concentration variations increasing the maximum emission wavelength and fluorescence intensity. In Figure 5, it can be seen that the change in Pb^{2+} fluorescence shows that the change in concentration has a relatively large effect on the selectivity of the sensor. The addition of heavy metal ions Pb^{2+} in the concentration range of $5x10^{-4}$-$5x10^{-7}$ M experienced an increase in fluorescence intensity (turn-on), namely the lighting effect increased with increasing concentration of Pb^{2+} metal ions [1]. This is because Pb^{2+} is an enhancing agent that is directly in contact with the probe (lanthanum complex compound) so that the fluorescence intensity increases. Enhancing agents in the form of heavy metals or diamagnetic elements such as Pb^{2+} are known to cause an increase in fluorescence intensity through the phenomenon of fluorescence enhancement. Diamagnetic elements have paired electrons in d orbitals such as Pb^{2+}, which gives rise to magnetic properties. The magnetic properties caused by diamagnetic elements are shown by the electromagnetic interaction of the ligand with metal ions Pb^{2+} which can produce lighting and cause fluorescence to increase in the maximum absorption region. This is known as the metal-enhanced fluorescence (MEF) mechanism. The sensitivity of the fluorosensor on lanthanum complex compounds with the addition of heavy metal ions Pb^{2+} can be affected by concentration, this is because the addition of metal ion concentrations of Pb^{2+} at a concentration of $5x10^{-4}$ M (the highest concentration) can give a response in the form of high fluorescence emission intensity as well.

The addition of heavy metal ions Cu^{2+} was carried out with several concentration variations, namely $5x10^{-4}$-$5x10^{-7}$ M into the La^{3+} complex compound with a concentration of $5x10^{-5}$ M using methanol-chloroform (1:1). In compounds that can emit light, electrons from the π* state do not relax directly to the ground state but undergo intersystem crossing towards the triplet state of the central metal ion. The appearance of the emission peak of the lanthanum complex compound at 470 nm indicates that there has been an emission from the LMCT (Ligand to Metal Charge Transfer) event from the excited state of the ligand (S1) to the La^{3+} ion with the electronic transition π*. At a wavelength of 370 nm with fluorescence intensity of 2925 a.u, a shift in wavelength in the 372 nm region occurs when the Cu^{2+} heavy metal ion is added, this is probably due to the addition of Cu^{2+} heavy metal ions with different concentration variations increasing the maximum emission wavelength and intensity its fluorescence.

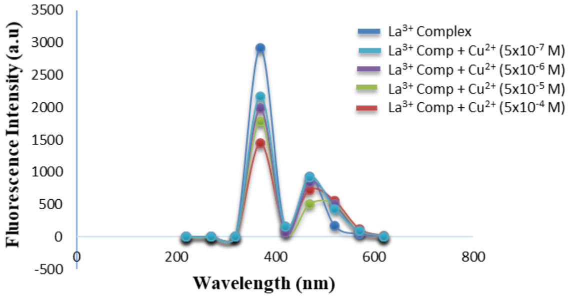

Figure 6. Fluorescence intensity spectrum of complex compounds on the addition of heavy metal ions Cu^{2+} at various concentrations

In Figure 6, it can be seen that the change in the fluorescence of Cu^{2+} shows that the change in concentration has a relatively large effect on the selectivity of the sensor. The addition of Cu^{2+} heavy metal ions in the concentration range of $5x10^{-4}$-$5x10^{-7}$ M decreased the fluorescence intensity (turn-off) [1]. The magnetic properties of metal affect the fluorescence intensity, Cu^{2+} metal ions are paramagnetic metals that tend to decrease the fluorescence intensity. The selectivity of fluorosensors based on complex compounds occurs because certain metal ions can significantly decrease or increase the intensity of organic fluorophores. The ability of metal ions to decrease or increase the fluorescence intensity of organic compounds is related to the electron configuration of the metal ions, where paramagnetic metals generally cause a decrease or decrease in fluorescence intensity, while diamagnetic metals tend to increase the fluorescence intensity. The addition of Cu^{2+} produces a blackout effect on the fluorescence intensity (turn-off). This is because Cu^{2+} metal is an extinguishing agent that is directly in contact with the probe (lanthanum complex compound) so that the fluorescence intensity decreases. Extinguishing agents in the form of heavy metals or paramagnetic elements such as Cu^{2+} are known to cause the extinction of fluorescence intensity through the phenomenon of intersystem crossing. Paramagnetic elements have unpaired electrons in their d orbitals such as Cu^{2+}, which give rise to their magnetic properties. The magnetic properties caused by paramagnetic elements can cause changes in the orientation of electrons in the excited orbitals in the molecules of compounds containing these elements, resulting in a triplet excited state. The return of the triplet excited electron to the ground state is forbidden according to the selection rules and is therefore slow. Due to the low emission velocity, the de-excitation process from this triplet state can be easily extinguished by Cu^{2+} ions [23].

Conclusion

The metal ion complex compound La^{3+} with the pyrazoline derived ligand has been successfully synthesized which can be seen from the characterization data. The melting point of the complex compound is 268.8 °C. The results of the fluorosensor study indicate that the metal ion complex compound La^{3+} with the pyrazoline derivative ligand has the potential to be used as a metal ion fluorosensor of Pb^{2+} type "turn-on" and Cu^{2+} type "turn-off". This heavy metal fluorosensor can detect the presence of Pb^{2+} and Cu^{2+} ions to a fairly low concentration of $5x10^{-7}$ M. On the addition of heavy metal ions Pb^{2+} and Cu^{2+}, there is a clear change in fluorescence which can be seen from a shift in fluorescence intensity and also an increase or decrease in fluorescence intensity, so it can be said that variations in concentration have a high effect on sensor sensitivity and selectivity.

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Author Contributions

All authors contributed to the researchand writing in this article.

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