

Review

Colorimetric Materials for Fire Gas Detection—A Review

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Abstract: The damage caused by outbreaks of fire continues to be enormous despite ongoing improvements in fire detection and fighting. Therefore, the detection of fires at the earliest possible stage is essential. The latest developments in fire detection devices include the addition of carbon monoxide (CO) or temperature sensors into the widespread smoke detectors, but also alternative solutions are searched for. Advantageous is the direct detection of the most relevant fire gases CO and nitrogen dioxide (NO₂), because they are produced very early in a developing fire. A sensitive, selective, and low-cost method to detect these gases is the use of colorimetric materials combined with a compact optical readout. In this review, we take account of recent developments in this research field and provide a comprehensive overview on suitable materials for CO and NO₂ detection in fire gas sensing and first steps towards novel fire gas detectors.

Keywords: colorimetric; sensor; fire gas; carbon monoxide; nitrogen dioxide

1. Introduction

In the case of fire, every second counts to prevent the loss of life. In addition, for each additional minute of response time, property damage increases by 2%. Widespread, state of the art sensors are smoke detectors which are often not adequate to alarm inhabitants quickly enough. Also heat detectors measuring the ambient air temperature are too slow to react. With both technologies, nonsmoking fires, e.g., pure ethanol fires, cannot be detected. A viable alternative is the use of systems relying on gas detection rather than particle detection. In particular, gas sensors provide a faster and more accurate fire detecting mechanism since gases are produced prior to aerosols in a developing fire (Figure 1).

Fire gas detectors, if available, are mainly installed in large automatic fire detection systems, and contain electrochemical cells for carbon monoxide (CO). Often these CO-detecting cells are added to smoke detectors [1,2]. Research efforts have focused on metal oxide-based (MOX) gas sensors for this application for many years [3–6]. Fire gas detectors containing MOX sensors are commercially available only for some niche applications such as caravanning, motor boats etc., because they suffer from high power consumption and a lack of selectivity. Also suspended gate field effect transistors (SGFETs) were proposed for fire gas detection in literature, but have not been marketed until now [7,8].

The detection of gases based on chemical reactions developing a visible color change was patented already in 1919 in the USA as a new type of gas detector [9]. Their main intention was to detect CO in small quantities by making use of the color change of iodine in the presence of CO. With the introduction of the so-called Dräger tubes[®] in 1937, this principle has begun to find widespread use in fire gas detection. These single-use glass tubes, containing the reactive colorimetric material, are broken

at one end upon use and permit a quantitative determination of the target gas. The concentration is read on a scale by the user.

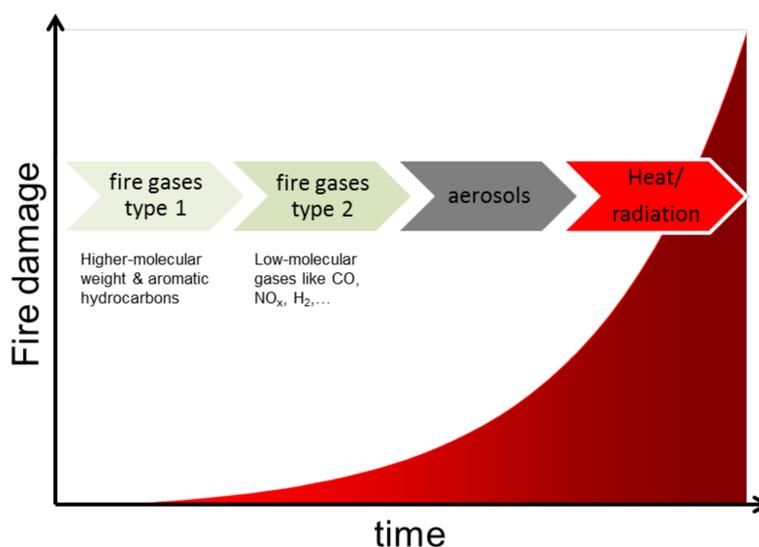


Figure 1. Scheme of the damage caused by fire outbreak occurring over time related to the fire indicators gas, aerosol, and heat/radiation.

Advances in the control of nanoparticles and synthesis of novel indicator molecules in combination with optical and micro-structuring methods now allow a conceptually new type of low-cost, ultra-low-power consuming fire gas detectors based on a colorimetric read-out. No other gas sensing principle for the specific detection of the two main fire indicator gases CO and nitrogen dioxide (NO₂) can achieve energy self-sufficient, battery-supported operation for up to 10 years. In the search for suitable colorimetric materials, further requirements for fire detectors regarding sensitivity and selectivity must be considered: based on the data available for typical test fires (burning wood, ethanol, polyurethane, *n*-heptane), relative humidities vary between 25% and 40%. In addition to CO₂, a significant increase of CO and NO₂ concentrations develop in all test fires. For CO, the background concentration (no fire) is 1–3 ppm, this value increases to 5–100 ppm depending on the type of fire. NO₂ is present in the environment in a background concentration of about 10 ppb and increases to 40 ppb to 3 ppm in the case of fire. Therefore, suitable colorimetric materials must yield detectable color reactions in the following concentration ranges:

- CO: 5–100 ppm
- NO₂: 0.4–3 ppm

Furthermore, the colorimetric materials must be stable for a long period of time (several years) when used for fire gas detectors, especially regarding thermal stresses, i.e., in the case of a fire, the color reaction must still take place. Also, the response time of a sensor based on the colorimetric principle must lie in the range of a few seconds to alarm the inhabitants quickly enough. These factors, i.e., response time, stability and reproducibility of such sensors are crucially influenced by the sensor configuration and the matrix the colorimetric material is embedded in. Especially the matrices are the topic of ongoing research due to their decisive role in a sensor intended to be commercialized. In the following, we review currently known or available colorimetric materials suitable for the detection of CO and NO₂ as relevant fire gases.

2. Materials for Carbon Monoxide Detection

The earliest description, dated back to 1928, of the colorimetric determination of CO in air or dissolved in blood can be found in [10]. The colorimetric material used there was iodine pentoxide (I_2O_5), which reacts with CO irreversibly as follows:



Since the liberated iodine is very easy to detect as a reaction product, this reaction is still used today in the Dräger tubes[®]. In comparison, Figure 2 shows the extensive technical equipment used for the same purpose scarcely one hundred years ago:

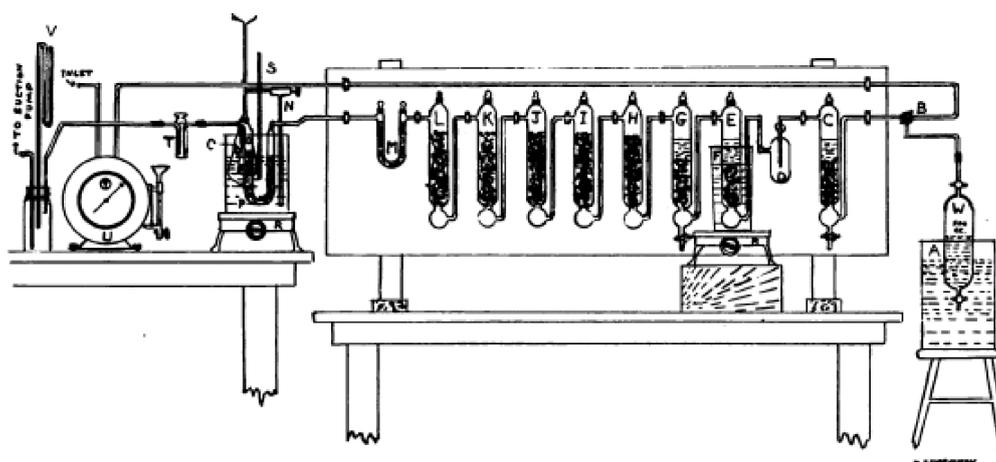
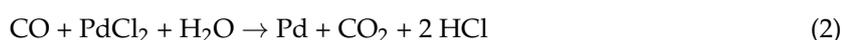


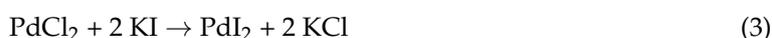
FIGURE I—APPARATUS FOR AIR ANALYSIS

Figure 2. Experimental setup for the determination of CO in air using I_2O_5 . Reprinted with permission from [10].

Martinek and his colleagues already reported a detection limit of 10 ppm in 1928, which roughly corresponds to the detection limit of the Dräger tubes[®]. About a decade later, the reaction of palladium(II) chloride ($PdCl_2$) with CO was described for the first time [11]:



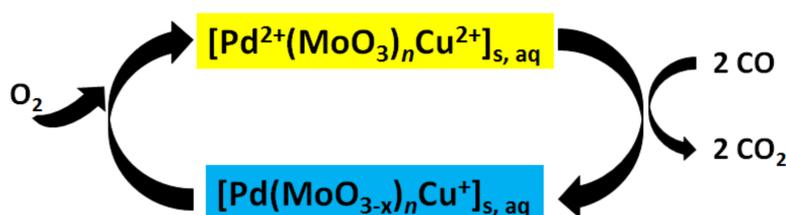
In this method, the concentration of unreacted $PdCl_2$ is subsequently determined using potassium iodide and the CO concentration is calculated therefrom.



However, the potassium iodide solution is relatively unstable, but can be replaced by other color indicators. Initially, the color reaction was determined using standard solutions of known concentrations. Later, this comparative method was replaced by spectroscopy [12]. At about the same time, a palladium-ammonium molybdate compound was proposed and patented for the determination of CO [13,14]. In this case, pure palladium is dissolved in sulfuric acid to produce palladium sulfate as catalyst. Ammonium molybdate hexahydrate $((NH_4)_6Mo_7O_{24} \cdot 4H_2O)$ is dissolved in water and added in about 30-fold excess to the palladium sulfate. The carrier or matrix used was silica gel. With this method, a yellow solution turns blue in the presence of CO (cf. reaction Scheme 1). A sensor based on this reaction was patented in 1984 by Herskovitz and colleagues [15]. In 1964, another method was published [16]: CO reacts in a basic solution with the silver salt of p-sulfaminobenzoic acid. The absorption of the silver colloid solution is determined spectrometrically and is proportional to the CO concentration. With this

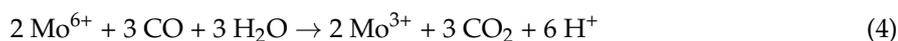
method it was possible to measure CO concentrations between 5 and 180 ppm with an accuracy of $95 \pm 5\%$.

Lambert and colleagues [17,18] also used palladium chloride to determine CO. The actual colorimetric determination, however, was accomplished by the reduction of the iron complex $[\text{Fe(III)EDTA}]^-$ to $[\text{Fe(II)EDTA}]^{2-}$. The latter compound triggers ligand exchange with $L = 2,2'$ -dipyridyl or 1,10-phenanthroline to form the stable $[\text{FeL}_3]^{2+}$ compound, the color of which can be determined spectrophotometrically in the blue/green wavelength range. Sodium molybdate was added as a catalyst. In further experiments they used, in addition to the palladium chloride compound, iodate and Leuco Crystal Violet (4,4',4''-methylidynetris(*N,N*-dimethylaniline)) which turns violet in the presence of CO, both as a function of the reaction time the CO concentration. Instead of Leuco Crystal Violet, a promazine hydrochloride complex, also in combination with palladium chloride, was described for colorimetric determination a few years later [19]. Another publication reports the use of pyronine-G, which is converted to benzene (also with PdCl_2 and iodate as base). The absorption of benzene is proportional to the CO concentration in a range of 20–400 ppm with a detection limit of 1 ppm [20]. Still in 1977, Shuler and Schrauzer patented a method for measuring reducing gases [21]. Here, a reversible reaction for CO determination was described for the first time: palladium sulfate serves as a catalyst for the intrinsically slow reaction of CO with ammonium molybdate, which changes from yellow to blue, and the reverse reaction with atmospheric oxygen to the ground state (Scheme 1). For the reverse reaction, a metal salt is needed (e.g., copper, iron, nickel chloride, sulfate, etc.).

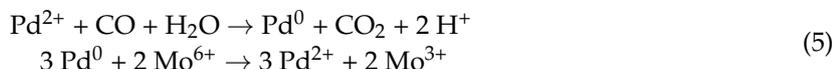


Scheme 1. Reaction scheme for the reversible detection of CO.

In a similar fashion, Goswami and colleagues patented in 1994 a specific and reversible CO sensor [22] based on molybdenum or tungsten salts with palladium salts as catalyst and metal salts for the reverse reaction. In general, the following redox reaction takes place:



This reaction proceeds only very slowly, therefore palladium salts are used as catalyst:



For the reverse reaction the metal salts, e.g., iron compounds, are used:



The atmospheric oxygen is sufficient for this reverse reaction, and the molybdenum compound regains its initial state and can react again. Another, relatively simple method was presented by Pal and colleagues in 1987 [23]. They used silver nitrate (AgNO_3) as an indicator in a gelatine solution and were thus able to determine CO in the concentration range of 2–100 ppm, with a standard deviation of 2.6% at 10 ppm CO.

Metalloporphyrins and metallophthalocyanines can also be used for the detection of CO. The reactions of these metal compounds with CO are reversible. Table 1 presents a compilation of currently known complexes:

Table 1. Metal complexes for the detection of CO.

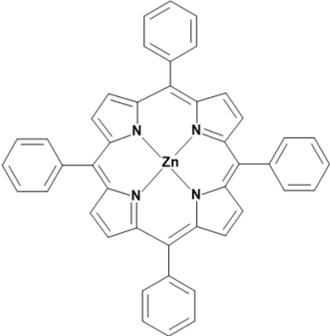
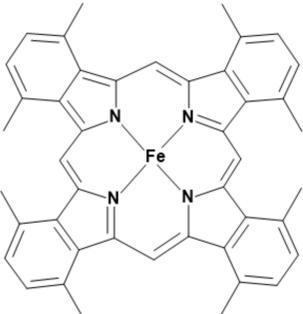
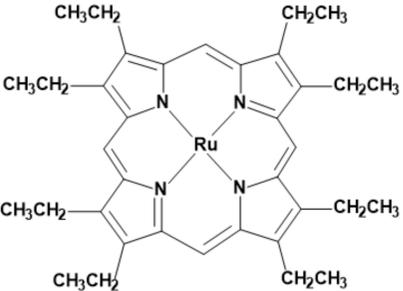
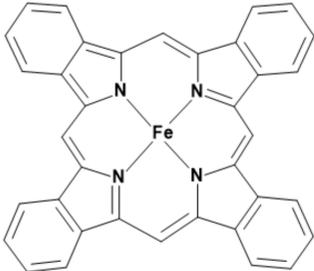
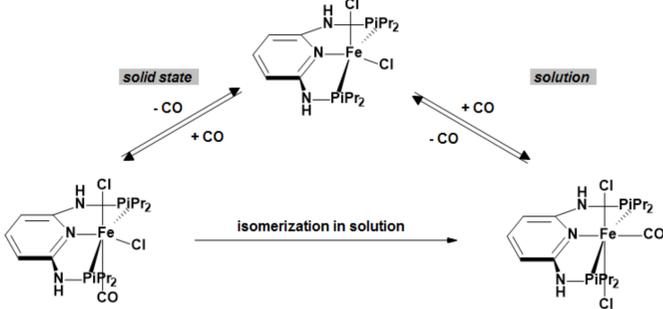
Complex	Description and Characteristics
 <p>(5,10,15,20-tetraphenylporphyrin) zinc</p>	<p>Upon binding of CO or NO₂, red-shifted absorption occurs. Details on stability or reversibility are not yet known [24].</p>
 <p>Octamethyltetrabenzoporphyrin iron</p>	<p>This compound is stable in the solid state and binds CO. In solution, a color change from green to red occurs. The compound is only stable in solution when pyridine is added as a stabilizer [25].</p>

Table 1. Cont.

Complex	Description and Characteristics
 <p data-bbox="465 651 779 678">Ruthenium porphyrin derivative</p>	<p data-bbox="994 485 1951 536">The CO-complexed molecule binds another CO reversibly and stronger than other porphyrins. There is no information about a color change [26].</p>
 <p data-bbox="510 983 734 1010">Iron(II) phthalocyanine</p>	<p data-bbox="994 836 1727 863">Binds CO and NO₂. It is thermally unstable (loss of amino functionality) [27].</p>
 <p data-bbox="524 1353 721 1380">Iron pincer complex</p>	<p data-bbox="994 1161 1899 1241">Extremely selective reaction with CO; no cross-sensitivities to NO or SO₂ are known. Complete regeneration is accomplished by heating at 100 °C for 5 min. No detailed information on gas sensitivities is available yet [28].</p>

Another promising material for CO detection is based on binuclear rhodium complexes. They show a fast and selective reaction towards CO and are completely reversible [29–31]. The general reaction scheme of the rhodium complexes $[\text{Rh}_2\{(\text{XC}_6\text{H}_3)\text{P}(\text{XC}_6\text{H}_4)\}_n(\text{OCR})_2] \cdot \text{A}_2$ with CO is shown in Figure 3. Table 2 gives the definition of possible ligands. An investigation of different rhodium complexes, obtained by varying the residues of the phosphines, regarding their reaction velocity towards CO exposure is published in [32].

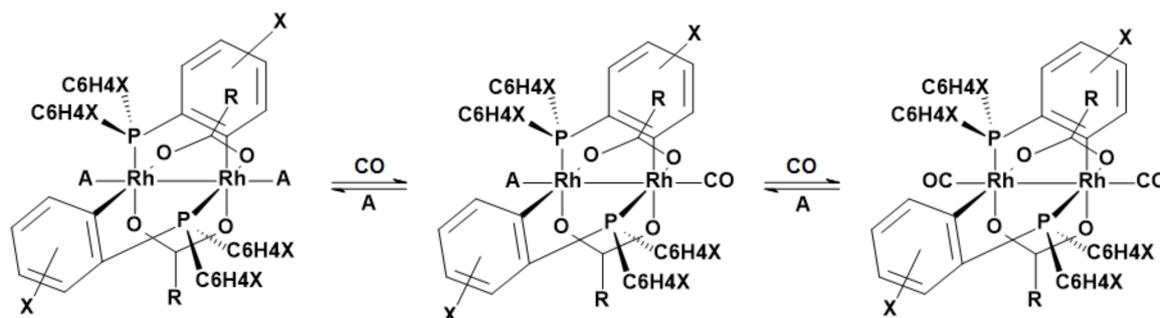


Figure 3. General two-step reaction scheme of the binuclear rhodium complex with the formula $[\text{Rh}_2\{(\text{XC}_6\text{H}_3)\text{P}(\text{XC}_6\text{H}_4)\}_n(\text{OCR})_2] \cdot \text{A}_2$. The color of the complex turns from violet to orange-yellow. Cf. Table 2 for the definition of the ligands.

Table 2. Ligands of the rhodium compounds 1·(A)₂–5·(A)₂.

Compound	X=	R=	A=
1·(A) ₂	4-OCH ₃	CH ₃	CH ₃ CO ₂ H
2·(A) ₂	3-CH ₃	CH ₃	CH ₃ CO ₂ H
3·(A) ₂	3-F	CH ₃	CH ₃ CO ₂ H
4·(A) ₂	4-OCH ₃ ; 3,5-CH ₃	CH ₃	CH ₃ CO ₂ H
5·(A) ₂	3-CH ₃	CF ₃	CF ₃ CO ₂ H

3. Materials for Nitrogen Dioxide Detection

Colorimetric materials for NO₂ can roughly be divided into three types: the first is essentially based on the *N*-(1-naphthyl)-ethylenediamine (NED) proposed by Saltzman in 1954 for the first time for NO₂ determination [33], the second of Jacobs and Hochheiser 1958 [34], and the third, on metal complexes. In the following the three classes are briefly described:

3.1. Saltzman Method

The Saltzman method originally uses a mixture of sulfanilic acid, NED, and acetic acid. Thus, a stable staining could be achieved upon contact of the solution with NO₂ with a detection limit of a few ppb. The solution had a low cross-sensitivity to ozone, for other gases it was negligible. The Saltzman method is one of the most sensitive colorimetric determination methods for NO₂ and has the advantage that all reagents are mixed in a solution and the color reaction develops over time. However, only a moderate long-term stability of the solution is also reported. However, this does not have to apply to an indicator layer in a suitable matrix, e.g., a polymer.

In detail, the reaction proceeds as follows: sulfanilic acid and NED form nitrite ions in contact with NO₂, which are detected by the color reaction. Nitrite reacts in acidic medium (acetic acid) to the nitrosyl cation:



The nitrosyl cation causes sulfanilic acid and NED to form an azo dye (red-violet). In this case, first a diazotization reaction takes place, in which a diazonium ion is formed; this is followed

by azo coupling (in the para-position to the NH_2 group of 1-naphthylamine). Figure 4 shows the partial reactions.

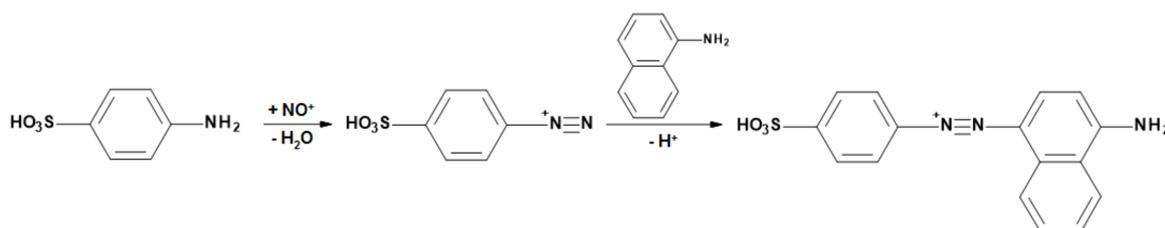


Figure 4. Partial reactions in the Saltzman method: the nitrosyl cation causes sulfanilic acid and NED to form an azo dye (red-violet). In this case, the first step is the diazotization reaction, in which a diazonium ion is formed; this is followed by the azo coupling.

Thomas and colleagues further developed the method and implemented a calibration because the color change reaction is not linear [35]. Further modifications of the Saltzman method can be found in [36,37]. Huygen [36] compared various azo dyes, including *N,N*-(1-naphthyl,acetyl) ethylenediamine-toluene monosulfate (ANEDA), *N*-(1-naphthyl)ethylenediamine dihydrochloride (NEDA), 1,8-diaminonaphthalene, 1-naphthylamine, and dimethylaniline. The first three yielded the best results. Nash [37] additionally added basic guaiacol solution to the reagents and buffered with glycerol. This resulted in a higher stability of the solution.

Smith patented a variation of the Saltzman method in 1972, in which a kind of paste was developed by addition of e.g., MgSO_4 and glycerol, and this paste was further processed into a pellet. As a result, the stability of the reagents could be further improved; moreover, this method allowed the measurement directly in air without the need for any equipment by means of a small sensor [38].

About 20 years ago, Tanaka and colleagues intensified the work on colorimetric NO_2 sensors [39–42]. Instead of NED, they used *N,N*-dimethyl-1-naphthylamine (NA) and, through the use of porous glass, also increased the active surface, which further increased the sensitivity of the sensors (<100 ppb). Figure 5 shows the structural formulas of the reagents used, Figure 6 shows an example of the absorption spectra of the reagents when exposed to NO_2 .

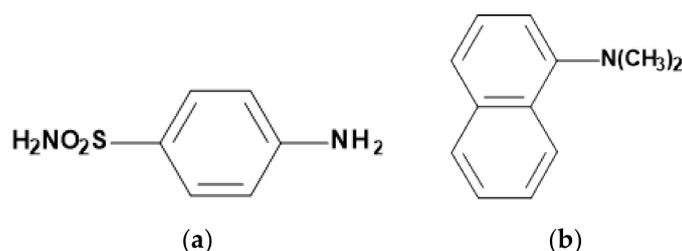


Figure 5. Structural formulas of (a) sulfanilamide (SA) and (b) *N,N*-dimethyl-1-naphthylamine (NA).

The investigation of further redox indicators from the group of aromatic amines is still ongoing: Alexy et al. used *N,N'*-diphenyl-1,4-phenylenediamine (DPPD), *o*-dianisidine, *N,N'*-diphenylbenzidine (DPB) and *N,N,N',N'*-tetramethyl-1,4-phenylenediamine (TMPD) immobilized in a gas-permeable polymeric layers for NO_2 sensing [43]. TMPD was found to be highly selective towards NO_2 with no cross-sensitivities to other relevant gases [44,45].

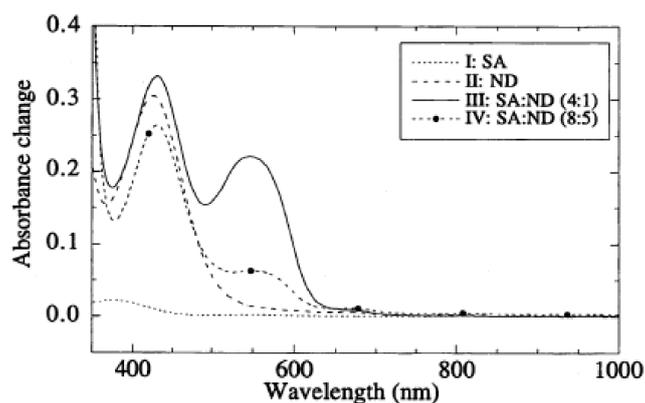


Figure 6. Absorption spectra of porous glass slides with Saltzman reagents, after exposure to 600 ppb NO_2 for 8 h (flow rate 1 L/min): with sulfanilamide (SA) (I), *N,N*-dimethyl-1-naphthylamine (ND) (II), SA and ND (4:1) (III), and SA and ND (8:5) (IV). Reprinted with permission from [39].

3.2. Jacobs and Hochheiser Method

In the Jacobs and Hochheiser method from 1958, 0.1 m NaOH is used as the absorption medium and the sulfanilamide is dissolved in phosphoric acid. The indicator, as in the Saltzman method, is NED. The colorimetric reaction is readout spectrophotometrically. This reaction was used in an automatic sequence sampler to monitor NO_2 emissions in urban areas on a 24 h basis. The reaction is also sensitive to sulfur dioxide, but when oxidized to sulfate by adding hydrogen peroxide, this does not interfere with the reaction. The limit of detection of the Jacobs and Hochheiser method is in the ppb range. Later, sodium arsenite was also used as the absorption medium, this being referred to as a modified Jacobs and Hochheiser method.

3.3. Metal Complexes

Similar to the detection of CO, also NO_2 can be measured using different types of metal complexes. Table 3 gives an overview of the metal complexes used for NO_2 detection that can be found in literature.

Table 3. Metal complexes for the detection of NO₂.

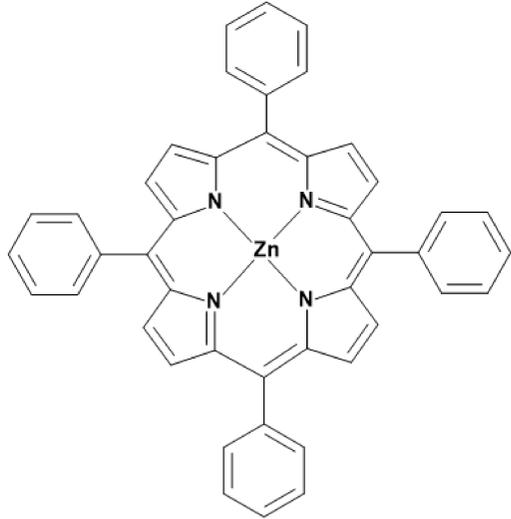
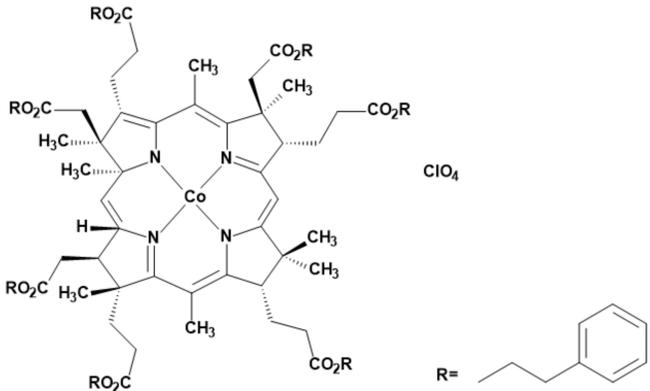
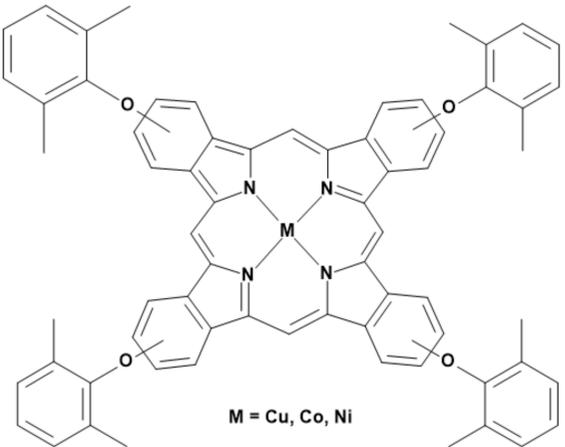
Complex	Description and Characteristics
 <p data-bbox="416 884 806 911">(5,10,15,20-tetraphenylporphyrin) zinc</p>	<p data-bbox="987 600 1973 655">Upon binding of CO or NO₂, red-shifted absorption occurs. Details on stability or reversibility are not yet known [24].</p>
 <p data-bbox="394 1334 828 1361">aquacyanocobalt(III)-cobyrinate derivative</p>	<p data-bbox="987 1102 1973 1185">Reacts very selectively to NO₂ but is not completely reversible. Captures a concentration range of 25–800 ppb within a few seconds. Was intended to be commercialized in a fire gas detector, but the compound turned out to be unstable from approx. 50 °C [46].</p>

Table 3. Cont.

Complex	Description and Characteristics
 <p data-bbox="555 751 685 772">M = Cu, Co, Ni</p> <p data-bbox="309 815 913 842">2,9,16,23-tetra(2,6-dimethylphenoxy)metalophthalocyanine</p>	<p data-bbox="987 555 1977 635">So far, only results on the reaction of Cu/Co. phthalocyanines on NO₂ exist, in which the conductivity is measured (no color change) [47]. The reaction is reversible. A detailed description of the chemical reaction (IR or Raman spectroscopic studies) upon binding of NO₂ can be found in [48].</p>

3.4. Other Methods

In 1984 Bajeva and colleagues presented another simple and sensitive method for the determination of NO₂ [49]: guaiacol is used in basic solution both as an absorption medium and a coupling reagent. With p-nitroaniline, a red dye is formed after the diazotization reaction. Information on the detection limit cannot be found here. Raman used benzidine in 1991 for the diazotization reaction with orcinol after NO₂ was absorbed onto sodium arsenite. This reaction causes a yellow color (460 nm), which can be detected spectroscopically [50]. The absorption according to Lambert-Beer is given as linear in the concentration range of 0.04–0.48 µg/mL nitrite [47].

A year later, Kaveeshwar and colleagues [51] published a similar procedure to Bajeva's: o-nitroaniline is used as an absorption and diazotization reagent. The red-violet color reaction results from coupling to 1-amino-2-naphthalene sulfonic acid (ANSA). Kumar and colleagues presented in 1993 a further modification of the above-mentioned methods [52]: they again used sodium arsenite as an absorption medium and p-nitroaniline and chromotropic acid in acetate solution for the color reaction. The resulting solution has a maximum absorption at 515 nm and is reported as linear in the concentration range of 0–20 µg/mL nitrite. This method was also compared with the Saltzman method, and the detection limit was determined to be 0.5 µg/mL. In Pandurangappa et al. also sodium arsenite as an absorption medium is mentioned [53]. The color reaction is based on the reaction of nitrite with aminophenyl benzimidazole in an acidic environment and NED as an indicator. The maximum absorption is 555 nm and is described as linear according to Lambert-Beer in the concentration range 0–10 µg in 25 mL solution. Parmar et al. [54] used, in addition to sodium arsenite as the absorption medium, aminoacetophenone in acidic solution and phloroglucinol as an indicator with an absorption maximum at 420 nm. The detectable concentration range is given as 0.008–0.12 µg/mL.

4. Conclusions

The present review shows the results of a literature search on currently known or available colorimetric materials for the detection of CO and NO₂; the focus was on their suitability for implementation in fire gas detectors. In principle, irreversible compounds are available for single-use sensors for CO such as iodine pentoxide in Dräger tubes[®], or reversible indicator molecules for long-term warning sensors, such as different binuclear rhodium complexes, molybdenum compounds with catalysts, or different (metallo-)porphyrins or (metallo-)phthalocyanines. Iron pincer complexes are promising, but their investigation is still basic research. For NO₂ detection, sensors based on azo dyes such as NED-based reagents or TMPD, have shown good results, but also metal complexes such as porphyrins or phthalocyanines. Table 4 summarizes the results.

Table 4. Summary of colorimetric compounds suitable for CO and NO₂ detection in fire gases.

Materials for CO Detection			
Compound	Reversibility	Measuring Range/Limit of Detection (ppm)	Cross-Sensitivity
Iodine pentoxide	irreversible	5–10	
Molybdenum complexes	reversible	2–100	n.a.
Metal complexes	Partly reversible	5–180	Towards NO ₂ , SO ₂
Rhodium complexes	reversible	10–200	
Materials for NO ₂ Detection			
Compound	Reversibility	Measuring Range/Limit of Detection (ppm)	Cross-Sensitivity
Organic dyes	Partly reversible	<0.1 ppm	Towards O ₃
Metal complexes	Partly reversible	25–800 ppb	Towards CO, SO ₂

Yet for an implementation in fire gas sensors, not only the gas sensing characteristics of the colorimetric compound itself is decisive, but also its long-term stability in changing environments, i.e., temperature and humidity variations. Also, hazardous compounds will probably not come into use (sodium arsenite, azo dyes). Another crucial influence on the sensing characteristics has the matrix in which the colorimetric material is embedded. The matrix must ensure gas permeability and, at the

same time, be thermally stable in a fire and insensitive to variations in the relative humidity in the environment. Further challenging is the response time of a sensor based on the colorimetric principle, which is influenced not only by the material itself, but also by the sensor configuration and the matrix. Sensor response times of a few seconds can be already achieved [32]. Future research should address the development of a matrix with the abovementioned characteristics, in combination with low-cost and compact optical sensors for read-out. This will play a vital role for the implementation of the colorimetric principle in commercial fire gas detectors.

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Conflicts of Interest: The authors declare no conflict of interest.

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