International Journal of GEOMATE, Aug. 2023, Vol. 25, Issue 108, pp.208-215
ISSN: 2186-2982 (P), 2186-2990 (O), Japan, DOI: https://doi.org/10.21660/2023.108.3892
Geotechnique, Construction Materials and Environment

TRENDS IN SENSORS AND METHODS OF MEASURING ATMOSPHERIC FORMALDEHYDE GAS CONCENTRATION: A PATENT LANDSCAPE

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ABSTRACT: Different methods and technologies of measuring atmospheric concentrations of formaldehyde have been proposed in recent years. When developing formaldehyde monitoring systems based on various sensors and technologies indoors and outdoors, emphasis is placed on such parameters as ease of operation, detection limits, cost, formaldehyde selectivity, and real-time monitoring. The patent landscape, an analysis that provides a snapshot of the patent situation of a specific technology, is applied to discover the trend of technologies that focus in a particular geography, industry, or a parent technology. Patent documentation on methods, technologies, and sensors designed to detect formaldehyde in the environment was searched for and analyzed The patent landscape was conducted, including the evaluation of patent documents by country, date, technology, methods, size, the automation of equipment, and patent classification by International Patent Classification. The study reveals that China has the largest number of registered patents. The market for patent technologies is principally dominated by analyzers for accurate and automatic determination of formaldehyde. Whereas electrochemical sensors are the most common technology used in sensor development.

Keywords: Monitoring, Formaldehyde, Sensor, Patent Landscape

1. INTRODUCTION

Air pollution has become an acute problem increasing public diseases and mortality [1]. The atmospheric air of cities contains a huge number of pollutants; the study focuses on formaldehyde (HCHO), a colorless gas with high chemical and biological activity. It can be found in indoor and outdoor air. Formaldehyde is widespread due to its numerous sources, such as industry [2], including building, woodworking, and furniture, textile, and carpet manufacturing [3], and its synthesis with volatile organic compounds (VOCs), including biogenic substances [4].

Formaldehyde monitoring is urgent because of its danger to human health [5,6]. The International Agency for Research on Cancer (IARC) categorizes formaldehyde as a Group 1 human carcinogen, causing nasopharyngeal cancer (PNC) and leukemia. About 3 % to 6 % of all cancers are caused by exposure to carcinogenic agents at the workplace [7,8]. Formaldehyde can also cause DNA damage and mutations in mammalian cells. Severe exposure can be harmful for health and cause irritation to the eyes, nose, throat, and skin [9] and reproductive system disorders [10].

Therefore, formaldehyde should be detected quickly and accurately using gas sensor technology. Formaldehyde coexists with a wide range of VOCs, including alkynes, alkenes, alkanes, alcohol, and halocarbons, which complicates the detection of a sensor reaction triggered by formaldehyde from other VOCs. Consequently, the detection specificity of formaldehyde compared to other VOCs must be increased, as selective detection has long been a problem.

Colorimetric and piezoresistive methods, electrochemical impedance spectroscopy (EIS) and metal oxide conductometry (MOX), are the most common methods of formaldehyde detection [11,12]. Despite the variety of methods available for the detection and measurement of formaldehyde gas, inexpensive, sensitive, and rapid analytical technology is still in demand.

Patent analysis, used to study different fields of science and technology, is one of the most reliable and important tools for obtaining technical and statistical information. Patent data are considered a good standardized and objective source measuring innovation activities. The patent landscape is the analysis of patents revealing technological trends. Based on patent documentation data, it has been a useful tool in recent times [13,14].

The purpose of this study is to by using the patent landscape methodology analyze and systematize the main trends in the patent protection of gas analyzers, methods, and equipment aimed at detecting formaldehyde in atmospheric air.

2. RESEARCH SIGNIFICANCE

Search for patent documentation, its analysis, and further patent landscape development represent an important and effective tool to evaluate changes in trends in qualitative and quantitative technologies of formaldehyde detection. Generally, the results of patent analysis describe the current situation in the international technology market and evaluate and guide policy proposals related to intellectual property rights [15] and innovations in formaldehyde monitoring.

3. MATERIALS AND METHOD

The search for patent documentation was performed using the Yandex and Rambler search engines, the All-Russian Patent and Technical Library, the Espacenet online service for searching patents and patent applications, and the PATENTSCOPE database. The scope of the patent search was 25 years, from 1998 to 2022.

The keywords for patent search were *formaldehyde + sensor*, *detection*, *detector*, *monitoring* and their combinations. However, they are associated with a large amount of information, thus making the analysis time-consuming and complex. This approach can potentially include wrong patents with too vague a wording. The use of IPC/CPC codes results in an extremely specific resolution of the study area, which prevents cross-cutting coverage of environmental technologies [16,17]. Therefore, in order to narrow the search, it was analyzed the result with an independent patent classification, which focuses the search, making it clearer and faster [18].

The patent documentation was searched on various search engines and databases; the final search results varied from 5,000 to 8,000 patents. At the final stage, the patents were analyzed according to their scope and screened for relevance.

The analysis was performed by evaluating the *title*, *abstract*, *claims*, *subject matter*, *technical concepts*, and *advantages* in the patent document reports. Sensors and equipment were not the only ones among the technologies considered, but also various methods, techniques, and materials capable of the qualitative or quantitative measurement of formaldehyde. The technology patents were analyzed in terms of the size of the device, the type (signal or accurate measurement) and the detection technology, the availability of automatic detection, the origin of the patent applicant, and the date of the patent publication.

4. RESULTS

4.1 Trends in Formaldehyde Detection Methods and Technologies

The study of the geographical patenting indicators on the territorial affiliation, namely the country of publication, of the patented technologies is shown in Figures 1 and 2.

China has had the largest number of formaldehyde analyzer patents in the last 25 years, accounting for about 75 % of all patents in the world. Japan and the US take the second and the third places with more than 7 % and 4 % of the total patents.

Patents have also been filed from Russia, India, Australia, Germany, and Korea. Patents were also registered by the World Intellectual Property Organization (WIPO) and the European Patent Office (EPO). The number of patents in Russia is insignificant and covers either the invention of sensors or methods of detecting; device design and industrial samples are hardly ever patented.

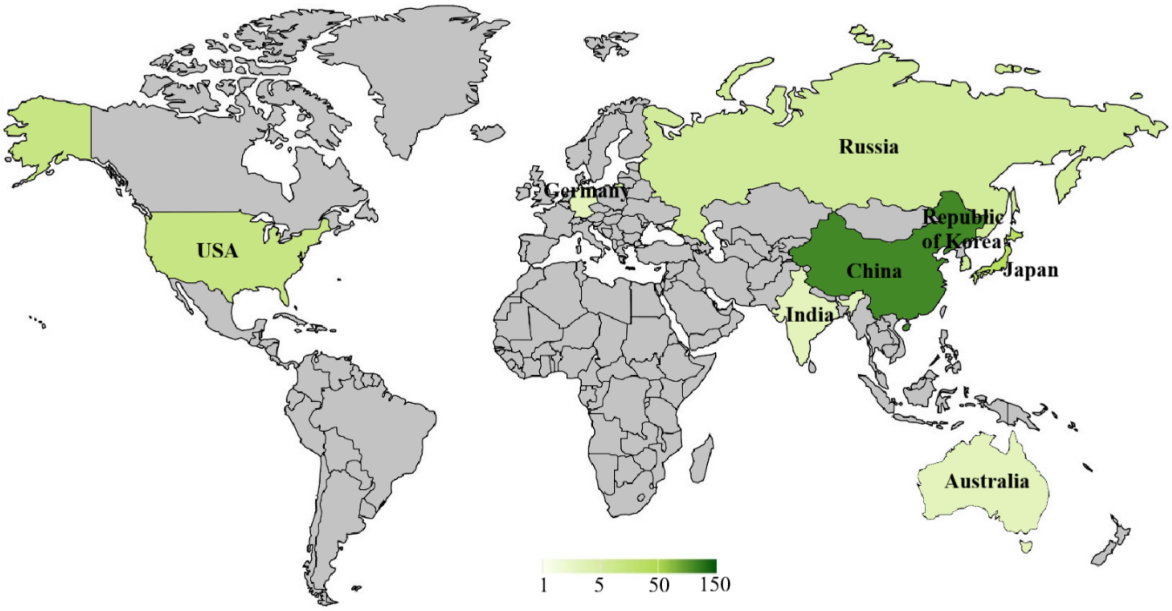

Fig. 1 Patent distribution by country

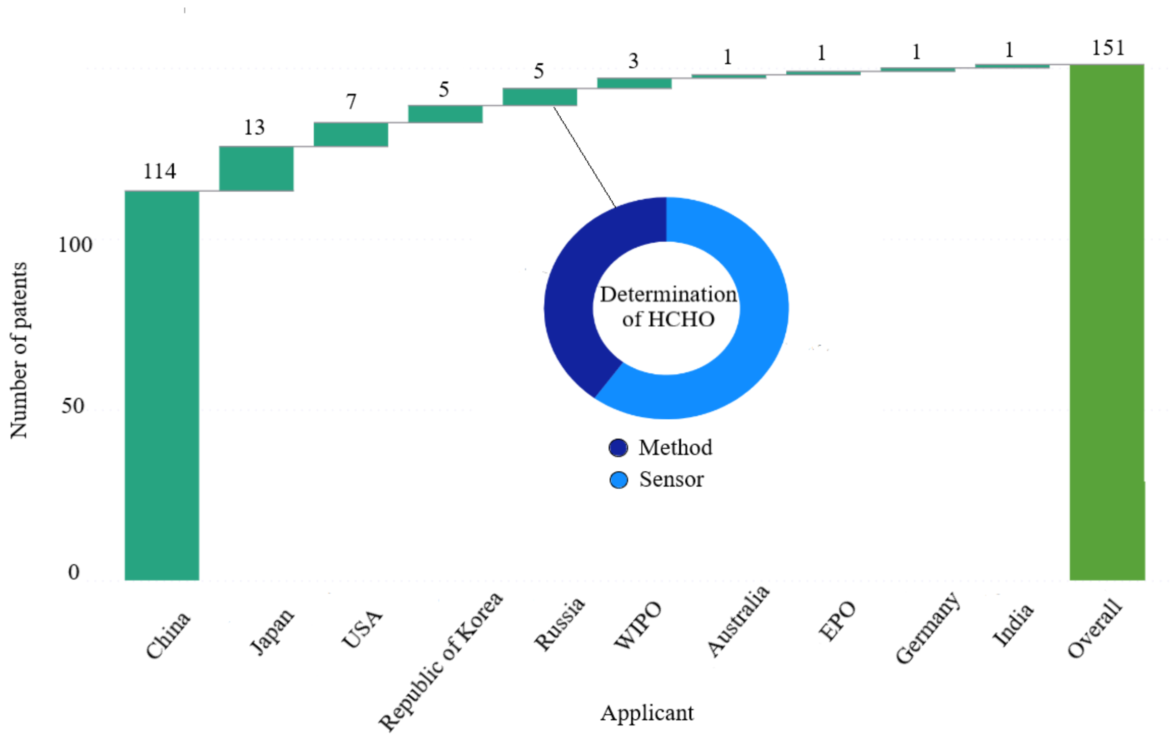

Fig. 2 Patent distribution by the main applicant

The largest number of registered patents was obtained in 2020 and 2021 – more than 12 % and 15 % of all analyzed patents, respectively. Over 10 % of intellectual property registrations of the total were made in 2018.

Figure 3 shows the surge in interest in analyzers and other formaldehyde detection methods patented in the last five to six years. Since the data analysis was done in mid-2022, the decline in patents number at this time is caused by the lack of some published patents at the time the patent landscape was set up.

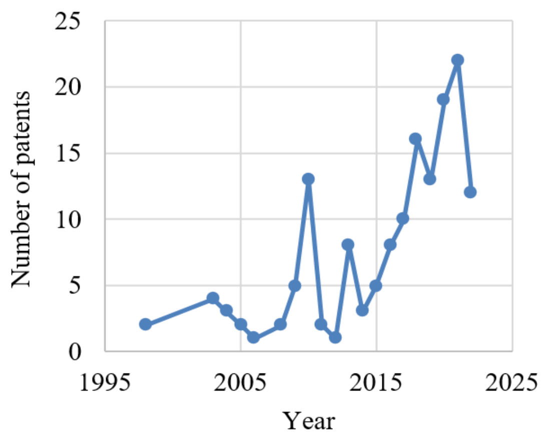

Fig. 3 Trends in the patent protection of technology from 1998 to 2022

Figure 4 shows the number of patent families in the countries and the average number of patents for an overall assessment. *Patent families* are a set of patents for the same invention issued anywhere in the world (the first publication is usually issued in the national patent office of the assignee), while the term *patent* includes only one patent document.

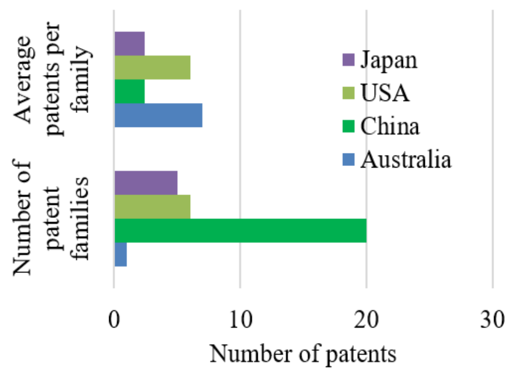

Fig. 4 The number of patent families and average number of patents per family

Figure 5 provides an overview of the technology classification according to international patent classification codes. The patents with the G01N code (Investigating or analyzing materials by determining their chemical or physical properties) represent a share of more than 80%.

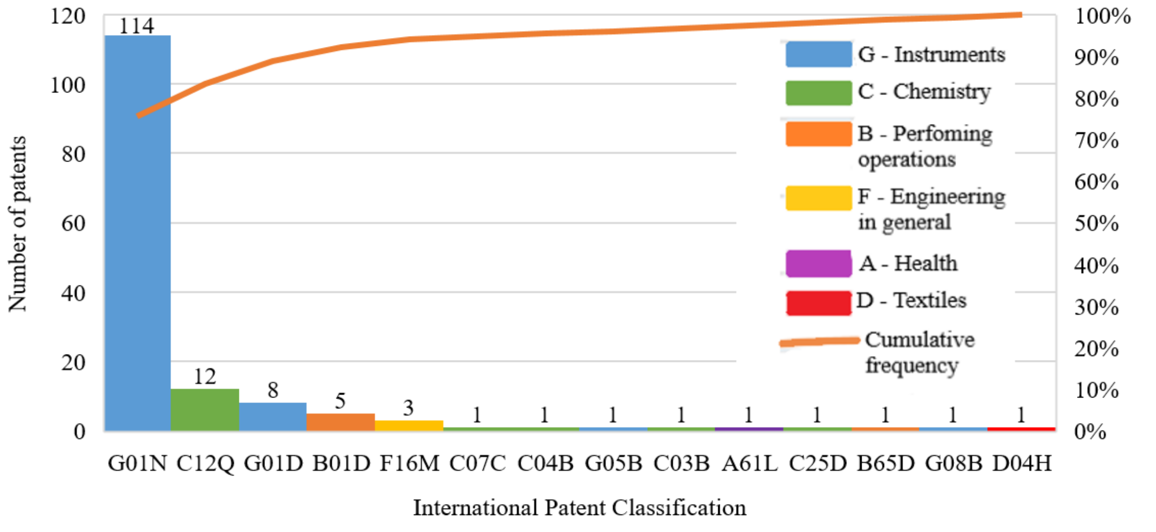

Fig. 5 Technology patents according to IPC

The frequently of international patent classification codes are listed in Table 1.

Table 1 The most frequently used international patent classification codes

Code	Meaning
G01N33/00	Investigating or analysing materials by specific methods
G01N27/12	Investigating or analysing materials by the use of electric, electrochemical, or magnetic means by investigating electrochemical variables
G01N27/407	Investigating or analysing materials by the use of electric, electrochemical, or magnetic means for investigating or analysing gases
G01N 35/00	Automatic analysis not limited to methods or materials; Handling materials therefor
C12Q1/26	Measuring or testing processes involving enzymes, nucleic acids or microorganisms, Compositions therefor; Processes of preparing such compositions (involving oxidoreductase)

More than 75 % of the inventions included this code, while the patents with C12Q (Measuring or testing processes involving enzymes, nucleic acids or microorganisms; compositions or test papers; processes of preparing such compositions); G01D (Measuring not specially adapted for a particular variable; arrangements for measuring two or more variables not covered in a single other subclass; tariff metering apparatus; measuring or testing not otherwise provided for) covered only 8 % and 5 % of all patents, respectively.

4.2 Types of Innovations: Characteristics and Special Features of Inventions

All the sensors were analyzed according to the following features: the availability of automatic detection (on-line detection without an operator), sensor portability, the type of detection (signal or precise), and the methods of detection. The greatest number of technologies are based on electrochemical sensors. The preference for electrochemical sensor systems can be because of their fast, accurate, selective, sensitive, and easy-to-use analytical tools for environmental sample analysis. They are efficient for detecting and monitoring pollutants in environmental samples because they require a very small sample volume for electrochemical analysis and use less energy than metal oxide-based sensors [19].

Modern electrochemical sensors use several properties to detect physical, chemical, or biological parameters. Some examples are environmental monitoring, health sensors, control and measuring devices, as well as sensors related to machines such as cars, airplanes, mobile phones, and transfer support. In addition to registering patents, Seo [20] proposed a formaldehyde gas sensor including a cantilever coated with a 3-mercatophenol self-assembled monolayer, where the sensor easily detects formaldehyde.

Many studies are being carried out on semiconductor sensors based on various metal oxides and bio-sensors, which can be used in various fields [21]. Recently, many formaldehyde gas sensors with sensitive materials made of micro- or nanoparticles, such as transducers, have been proposed. The analysis of these methods is shown in Figure 6.

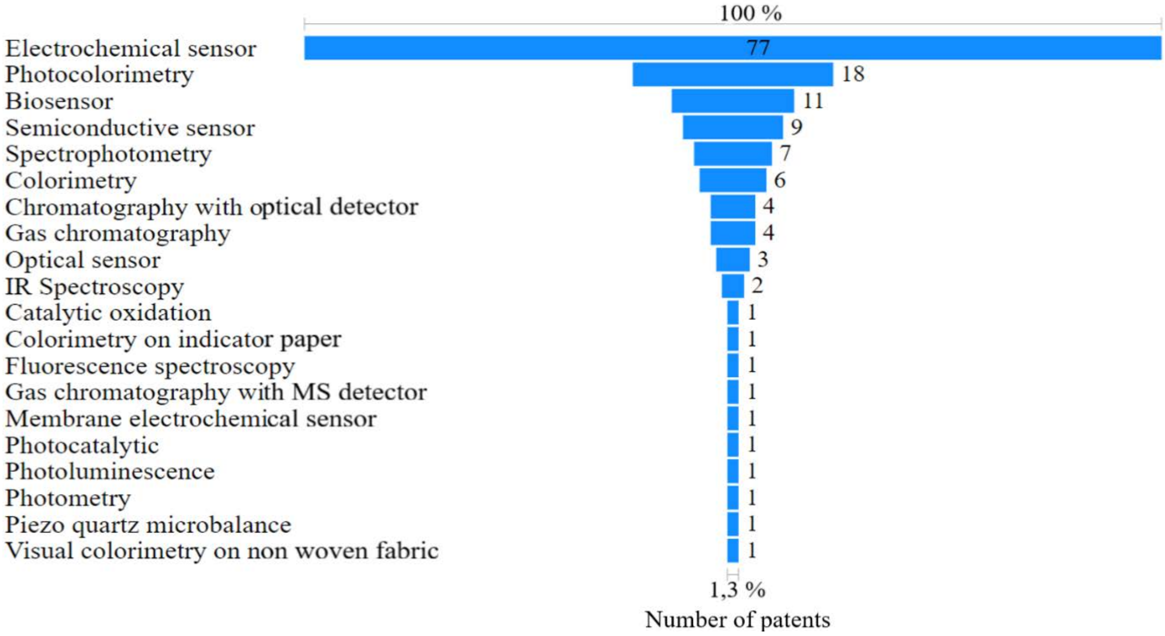

Fig. 6 Patent distribution according to the detection method

Table 2 Reagent kits and methods for formaldehyde measurement by Suzhou Anj Biotech

Publication	Main ingredients of reagent kit
CN107340289A	buffer solution, coenzyme, catechol, magnesium chloride, formaldehyde dehydrogenase, hydrogenlyase, chlorobenzoic acid-1,2-dioxygenase and stabilizing agent
CN101793781A	buffer solution, coenzyme, ferricytochrome, catechol, magnesium chloride, formaldehyde dehydrogenase, hydrogenlyase, chlorobenzoic acid-1,2-dioxygenase and stabilizing agent
CN101793786A	buffer solution, coenzyme, acetyl-coenzyme A, formaldehyde dehydrogenase, formic acid C-acetylase, coenzyme A-disulfide reducase and stabilizing agent
CN101793789A	buffer solution, coenzyme, acetaldehyde, coenzyme A, formaldehyde dehydrogenase, lactic acid aldolase, lactic dehydrogenase, pyruvate dehydrogenase and stabilizing agent
CN101793782A	buffer solution, coenzyme, acetyl-coenzyme A, acetaldehyde, formaldehyde dehydrogenase, formic acid C-acetylase, acetaldehyde dehydrogenase and stabilizing agent
CN101793779A	buffer solution, coenzyme, catechol, magnesium chloride, formaldehyde dehydrogenase, hydrogenlyase, chlorobenzoic acid-1,2-dioxygenase and stabilizing agent.
CN101793785A	buffer solution, coenzyme, acetyl-coenzyme A, glutathione, formaldehyde dehydrogenase, formic acid C-acetylase, coenzyme A-glutathione reductase and stabilizing agent
CN101793787A	buffer solution, coenzyme, adenosine triphosphoric acid, dihydrofolic acid, glyceric aldehyde-3-phosphoric acid, formaldehyde dehydrogenase, formic acid-dihydrofolic acid ligase, glyceric aldehyde-3-glycerol phosphate dehydrogenase and stabilizing agent
CN101793784A	buffer solution, coenzyme, acetyl-coenzyme A, 3-formyl acetic acid, formaldehyde dehydrogenase, formic acid C-acetylase, malonic acid-succinate semialdehyde dehydrogenase and stabilizing agent
CN101793788A	buffer solution, coenzyme, adenosine triphosphoric acid, tetrahydrofolic acid, glyceric aldehyde-3-phosphoric acid, formaldehyde dehydrogenase, formic acid-dihydrofolic acid ligase, glyceric aldehyde-3-glycerol phosphate dehydrogenase and stabilizing agent

Advances in nanotechnology have introduced one-dimensional or two-dimensional nanoscale materials, such as metal oxide nanowires, which have recently been used as the sensing layers in chemical gas sensors [22]. Their special structure and morphology, free of grain boundaries in single nanowires, give them long term stability. They are also characterized by a small cross section of conduction channels and porous morphology. Thus, these sensors are effective due to their improved properties such as a high a surface-to-volume ratio, hypersensitivity, better selectivity, and a rapid response.

The use of polymer-based sensing layers is another promising approach for formaldehyde gas sensor development due to their high sensitivity, short response time, reversibility, and performance at ambient temperatures. Polymers, typically in the form of solid thin films, are used as sensing media in a variety of solid-state gas and liquid sensors because they are easy to make and their properties can be adapted to a given application.

Aldehyde dehydrogenase (ALDH) and formaldehyde dehydrogenase (FALDH) are commonly used in the design of formaldehyde biosensors with diaphoretic and electrochemical mediators. The main advantage of using biosensors based on NAD-dependent (nicotinamide adenine dinucleotide) dehydrogenase (a cofactor of the enzyme) is that O_2 does not prevent formaldehyde detection, since it is not involved in the reaction [23]. In biosensor and enzyme colorimetric technology, the Chinese firm Suzhou Anj Biotech CO LTD has patented 10 reagent kits, for measuring formaldehyde concentrations. A detailed description of each patent is provided in Table 2.

Different technologies by size, type of detection, and automation, given in Figures 7–9, were analyzed. According to the data, more than 71 % of all patents deal with automatic sensors.

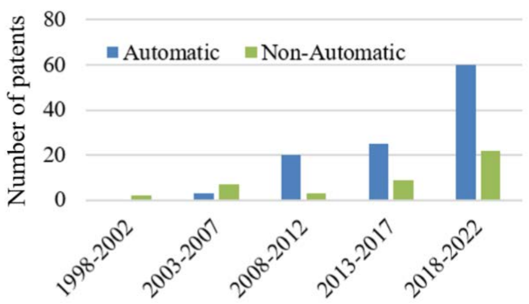

Fig. 7 Technology distribution according to the availability of automation

The sensors with precise measurement prevail over signal notification (80 % and 20 %, respectively). The patent field in the area of non-signal and automatic (enabling measurements without operator involvement) formaldehyde analyzers is vacant.

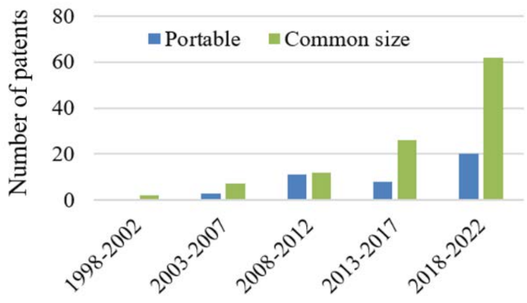

Fig. 8 Technology distribution according to size

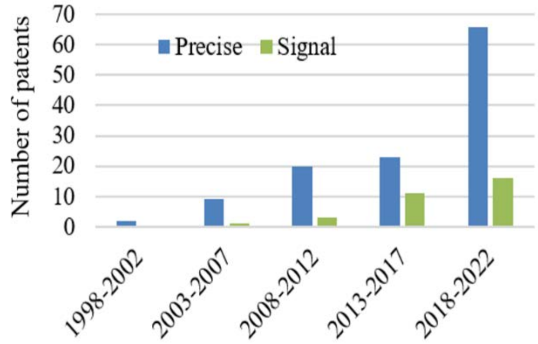

Fig. 9 Technology distribution according to the type of formaldehyde detection

5. CONCLUSION

The development of sensitive, specific, low-cost, and reliable methods of real-time monitoring has become increasingly important, therefore the research results help assess the current state of formaldehyde detection. Due to recent technical advances, a wide range of sophisticated sensors are being produced. Numerous detection methods (electrochemical, gas chromatographic, optical, chemiluminescence colorimetric) have shortcomings. Thus, sensor technologies are essential for concise and accurate formaldehyde detection onsite and in real time. The patent data revealed that most research is focused on studying and developing electrochemical and semiconductor sensors, which are highly sensitive, low cost, and have a rapid response rate. In order to improve their performance, there is a great deal of research on semiconductor gas sensors to be refined and registered soon. The patent landscape evaluated patenting trends over the past 25 years and identified the growth of patents for formaldehyde sensing technologies, the specification of technologies, the classification, and the geographic distribution of patent activity. The results may be of interest to academic circles, industry, and national governments.

6. ACKNOWLEDGMENTS

The project was funded by Russian research and production Company TEKO.

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