Research of the features of measuring ozone-depleting substances

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Abstract. Monitoring of ozone-depleting substances takes place in global climate policy. To ensure accounting of used and transported ozone-depleting substances, it is necessary to develop high spectral identification systems. Multicomponent refrigerants with a high ozone-depleting potential and a potential for global warming are considered as ozone-depleting substances. The features of refrigerants as objects of research are described. Based on the characteristics of refrigerants, such identification methods as chromatography-mass spectrometry, absorption spectroscopy and Raman spectroscopy were reviewed. Comparative analysis of refrigerant identification methods has been performed. According to the results of the data obtained in the analysis of refrigerants, the Raman spectroscopy method was chosen as the most selective one. The block-diagram for the identification system for ozone-depleting substances was proposed and experimental studies of the refrigerant R-22 were carried out.

1. Introduction
Monitoring of ozone-depleting substances and greenhouse gases has become a significant challenge in the green policy. According to the Montreal Protocol on Substances that Deplete the Ozone Layer, it is necessary to ensure the withdrawal from the use of substances such as chlorofluorocarbons (CFC) and hydrochlorofluorocarbon (HCFC). Based on the Kigali Amendment, it is also necessary to reduce the number of hydrofluorocarbons (HFC) used. All these substances are widely used as refrigerants in air conditioning and cooling systems [1]. A well-known example of ozone-depleting substances refrigerant R-245fa is classified as HFC and has global warming potential (GWP) for about 1030 years. In that case, legal regulation of the use of refrigerants is developing as significant part of climate policy [2].

According to local government documents and standards there is a need for systems for identifying refrigerants during cross-border transportation, production, and storage. Since 2021, there is a 20-year government plan to reduce the number of greenhouse gases that begin to operate in the Russian Federation. This plan pay high attention to using and transiting HFCs. It is important to have the opportunity for determining such kinds of substances in case of toxic combustion products of refrigerants for all living organisms.

Recent research has suggested that modern refrigerants such as R-1234yf or R-1234ze have more complicated structures [3]. According to physical state and characteristics of refrigerants, there are a lot of methods that can be implemented in analytical installations. However, most installations can
only identify a limited number of refrigerants. This case of ozone-depleting substances demonstrates the need for high spectral analysing systems [4].

The goal of this work was to compare methods of identification for developing a high spectral analysing system for ozone-depleting substances. For the widespread control of ozone-depleting substances, it is necessary to introduce systems for the identification of working substances like refrigerants in the services of maintenance and production. Therefore, it is necessary to follow the description of the refrigerants and their characteristics to formulate the requirements for the installation.

2. Materials and Methods
To perform the modelling of the identification system for ozone-depleting substances, description of investigated objects was performed. A refrigerant is a fluid used to transfer heat in compression refrigerating engineering units by changing its physical state. According to standard ISO 817-2014 “Refrigerants. Designation system”, there are several groups representing the greatest danger when released into the atmosphere. The description of the groups of refrigerants was carried out and the most common refrigerants were identified as working substances.

The following methods of identification of substances were investigated in the work: chromatography - mass spectrometry, absorption spectroscopy and Raman spectroscopy. Operating principles and technical solutions in the field of ozone-depleting substances analysis were reviewed. To assess the efficiency of identification methods, it is advisable to consider the data obtained.

3. Results and Discussions
In terms of chemical composition, refrigerants are haloalkanes, chlorine and fluorine-containing derivatives of saturated hydrocarbons (mainly methane and ethane), used as refrigerants in refrigerating engineering (for example, in air conditioners) [5].

Most common refrigerants have high ozone depletion potential (ODP) and GWP values. The current challenge is the conversion to ozone-friendly refrigerants with an ODP of 0 and a relatively low GWP [6]. The list of the most common manufactured and imported refrigerants regulated on the territory of the Russian Federation is presented in Table 1.

Table 1. Refrigerants regulated by the government of the Russian Federation for movement across borders, within the country, in places of production and consumption.

| Name | Type  | ODP | GWP  | Molecular mass | Boiling point at atmospheric pressure, °C |
|------|-------|-----|------|----------------|------------------------------------------|
| R-11 | CFC   | 1   | 4750 | 137.4          | 24                                       |
| R-12 | CFC   | 1   | 10890| 120.9          | -30                                      |
| R-21 | HCFC  | 0.05| 1850 | 102.9          | 9                                        |
| R-22 | HCFC  | 0.05| 1760 | 86.5           | -41                                      |
| R-125 | HFC | 0   | 3500 | 120.0          | -49                                      |
| R-134a | HFC | 0   | 1430 | 102.0          | -26                                      |

Refrigerants are multi-component substances and complex mixtures. Due to a huge number of identifying composition and low concentrations, measuring systems must be highly selective.

It is a widely held view that the method of chromatography-mass spectrometry is the most accurate way of identification [7]. A serious weakness with this argument, however, is that such method has cross-sensitivity of spectra and sample destruction [8]. Also, chromatography-mass spectrometry method demand takes a lot of time.

Absorption spectrometers are the most common instruments for refrigerants identification. Based on patent analysis, significant number of technical solutions used method of absorption spectroscopy. The method feature result in the study of the absorbed wavelengths of investigated substances.
However, this method also has spectral overlap. Therefore, absorption spectrometers can detect limit numbers of refrigerants [9].

In contrast to the previous methods, Raman spectroscopy has a higher resolution compared with chromatography-mass spectrometry. There is no overlap of the spectra of the samples in Raman spectrometers. A significant advantage of Raman spectroscopy is a high speed for analysing substances without destroying the sampler structure [10].

Comparison of refrigerant identification methods is shown in Table 2.

Based on the results of the analysis, it was concluded that the method of Raman spectroscopy should be used to develop a system for identifying ozone-depleting substances. Raman spectroscopy is presented on the study of the scattered light from a sample according to electronic transitions between vibration levels. Based on experimental data, ozone-depleting substances require spectral resolution up to 10 cm$^{-1}$ for frequency selectivity.

### Table 2. Comparison of refrigerant identification methods

| Method                        | Minimum detectable concentrations, % | Advantages                                    | Disadvantages                          |
|-------------------------------|--------------------------------------|-----------------------------------------------|----------------------------------------|
| Chromatography-mass spectrometry | 0.00001-0.01     | Arbitration method for analysis of refrigerants | Sample is destroyed. Spectral overlap   |
|                               |                                      | Determination of complex mixtures             | Frequent recalibration                  |
|                               |                                      | Determination of mass concentrations         | Long analysis time                     |
| Absorption spectroscopy       | 0.00001-0.1      | Simple construction                           | Source dependence                      |
|                               |                                      | Speed of data processing                      | Spectral overlap of complex mixtures,   |
|                               |                                      | Long interval between calibrations            | Cross-sensitivity                      |
| Raman spectroscopy            | 0.000001-0.001  | Unique characteristic of each substance       | Weak signal                            |
|                               |                                      | Speed of data processing                      | Need to exclude Rayleigh scattering    |
|                               |                                      | Intense signal from symmetrical vibrations    |                                        |

According to requirements, a block diagram of the high spectral analyzing system for ozone depleting substances was developed (Fig. 1).

![Figure 1. Block diagram of high spectral analysing system for ozone depleting substances](image)

The algorithm of installation operation includes the phased use of lasers. The laser source generates monochromatic coherent radiation. With the help of the optical system, laser radiation reaches the sampler. In the sampler, analyzing refrigerant is converted into liquefied gas at the temperature of 20 °C. Scattered radiation from the sample reaches the filter system. The filter system includes two filters that exclude Rayleigh radiation. The remaining Raman scattering is detected by the spectrometer. Processing and analysis of Raman spectra is performed on personal computer. After using the first laser with a wavelength of 785 nm, the algorithm repeats with a laser of 532 nm.

The findings of this study suggest that is necessity to create own library of Raman spectra. As shown by experiments with a laser light source at 785 nm, the spectrometer must record the Raman spectra from 200 to 1050 cm$^{-1}$ (Fig. 2).
4. Conclusion
The description of refrigerants classified as ozone depleting substances has been carried out. The analysis of methods for identification of ozone-depleting substances included chromatography-mass spectrometry, absorption spectroscopy and Raman spectroscopy. The method of Raman spectroscopy was chosen as the most accurate method for the determination of complex mixtures. Based on the characteristics of refrigerants, a diagram of an analytical installation including two radiation sources was proposed. Experimental data have shown the possibility of identifying symmetric vibration modes of atomic bonds of refrigerants.

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