

ISOTOPIC-SPECTRAL DETERMINATION OF CARBON IN HIGH PURITY INORGANIC MATERIALS

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Abstract: Isotopic-spectral method [1] was applied for determination of carbon in silicate materials (pure silica, quartz glasses, geological probs etc.).

Isotopic heterogeneous balancing of carbon in gaseous phase and solid samples was carried out at the temperature of 1500-1900°K.

Spectroscopic measuring of isotope concentration in a balanced gas was made using the electron-vibrational band heads of CO molecules excited in HF discharge.

Limits of detection of carbon concentrations appear to be $n \cdot 10^{-6}$.

Keywords: Isotopic-spectral method, heterophase balancing, isotopic composition measurement [1].

1. Introduction

Detection of small quantities of admixtures of carbon in silicate materials is in fact a very complicated problem. At the same time, the interest to and the need in the efficient solution of the problem became more keen recently because of the problem of synthesis of pure silicate matter and of geochemical investigations.

The difficulties in solving the said problem lie in that silicate materials represent actually a wide range of objects to be investigated which often have very difficult physical and chemical characteristics. Consequently, the results of the analysis demonstrate severe dependence on both composition of specimens and condi-

tions of detection. Application of standard specimens identical in composition with specimens to be analysed may probably show the way out of difficulty. However, creation of specimens suitable for a great number of various objects constituted a particularly unsolvable problem. Speaking about application of spectral methods of analysis, it should be pointed out that the great difficulties in selecting the homological analytical lines or strips will inevitably be faced here.

The isotopic-spectral method utilizing the rare stable isotopes of elements in question having very close properties and almost ideally homologous analytical spectra as the inner standard allows to overcome the

difficulties mentioned in [1]. The principle forming the basis of the heterophase balancing of isotopes of the elements to be determined (C in our case) in the «solid specimen to be analysed - gas» system with subsequent determination of the isotopic composition of the element in question the **balanced gas phase**. Upon attaining the equilibrium realized by heating the system, there appears a very complex set of chemical states of isotopes in both solid specimen and gas phase. However, it may be affirmed that relative concentration of isotopes for all those states of the element being determined are the first approximation the same. In this case, measurement of such parameters as mass of the specimen, quantity of gas admitted, relative concentration of widespread and rare isotopes in the gas phase both before and after the balancing makes it possible to solve the analytical problem of determining the admixture in the solid specimen.

2. Experimental

The carbon isotopic composition measurement has been carried out in the spectroanalytical plant with

photoelectric registration of intensities of isotopic components of the electron-oscillatory regions of molecules (483.5 nm, 519.8 nm) singled out with the help of the monochromator (dispersion 0.4 nm/mm). The gas glow was initiated by the high-frequency electrodes discharge (ab. 0.3 kW; ab. 1.67 MHz) in the quartz discharge tube with inside diameter of about 1 to 4 mm and about 80 mm long. The relative intensity of edgings of the analytical regions of isotopic components was measured with due allowance for their transpositions. The relative concentration of isotopes was obtained from the calibration charts (Fig. 1).

For obtaining the best signal-to-background intensity ratios, the investigations have been carried out on optimizing the conditions the spectroscopic measurements are carried out under (quantity of the analysed gas, degree of its dilution with the inert gas - the discharge carrier, pressure and so on).

Basing on the results of investigations, the carbon spectroscopic isotope analysis techniques have been developed which allow to perform the isotopic analysis in:

- pure gases: CO, CO₂ in the amount from about 10⁻⁴ ml under normal conditions and over;
- mixture of CO (CO₂) with helium - discharge

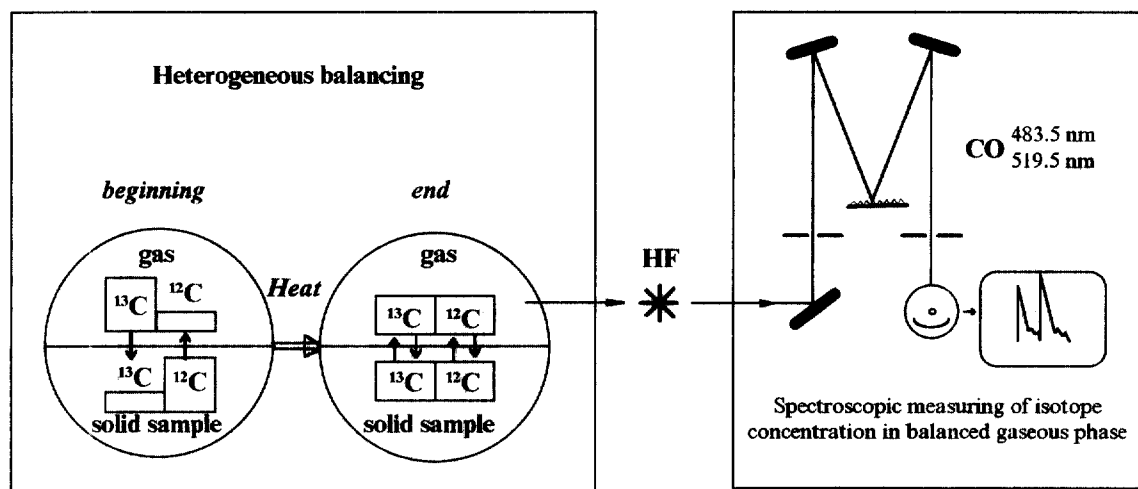


Fig. 1 Diagram of applying the isotopic-spectral method for C detection in silicate materials.

carrier. In this case the analysed gas minimum amount can be reduced to about 10^{-6} ml under normal conditions.

The carbon isotopic analysis accuracy realized with $^{12}\text{C}/^{13}\text{C}$ relative concentrations ranging from 0.2 to 5.0 is characterized by the relative standard deviation value of 0.02 - 0.05.

Correctness of the results obtained has been checked with the help of synthetic mixed gases.

The heterophase balancing of carbon isotopes has been carried out at a temperature of about 1500-1900 °K. The balancing temperature has been setup by 50-100°K below the analysed object fusion point. A molybdenum crucible with alundum or molybdenum tin pro-

TECTIVE inserts and with the cover was placed inside the cooled quartz reactor (exchanger). The crucible with finely dispersed specimen was heated up by HF currents. We used the high-frequency oscillator, 15 kW, with 440 kHz operating frequency [2].

For silicate materials with comparatively low fusion temperature, the heterophase balancing of carbon isotopes may be carried out in the resistance furnace with the specimen placed directly into the quartz exchanger. In this case, however, the heating temperature cannot exceed 1300°K and balancing takes more time.

Fig.2 shows the devices for carrying out carbon isotopes heterophase balancing in silicate materials.

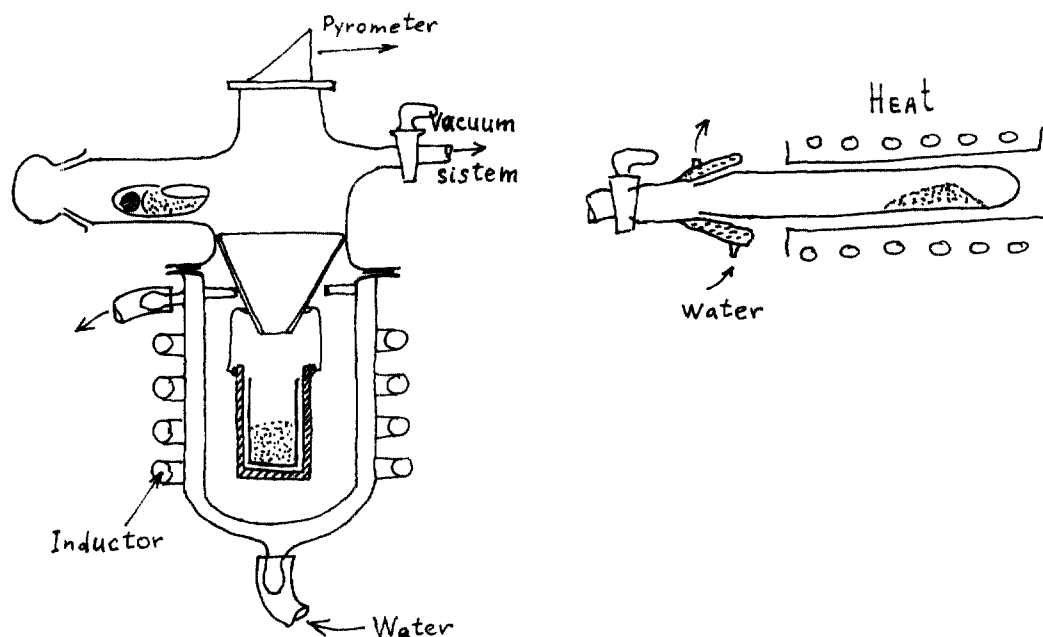


Fig.2. Exchangers for carbon isotopes heterophase balancing in silicate materials.

3. Results and Discussion

The analytical potentialities of various methods of carrying out the carbon isotopes heterophase balancing have been studied in details in all the cases mentioned. Series of investigations has been carried out in what concerns the kinetics and completeness of carbon iso-

topes heterophase balancing in the most widespread compounds of these elements, especially in the most strong of them. The results of such investigations formed the reliable basis for optimizing the conditions to ensure completeness of isotopes heterophase balancing within the widest range of silicate materials. Also investigated were the kinetics and completeness of the isotopic

exchange between gases CO_2 and finely dispersed specimens of carbides (TiC, SiC, TaC, NbC, Mo_2C , Fe_3C , ZrC, WC), carbonitride (TiCN), carbonates (CaCO_3 , K_2CO_3 , NaCO_3).

The investigations covered also the kinetics and completeness of carbon isotopes heterophase balancing in various silica modification (quartz, cristobalite, quartz glasses of various synthesis, synthetic silicon dioxide) as well as in various granitoids (granodiorites, biotithornblende and biotitmuskovate granites).

Basing on the investigations carried out, the methodical recommendations have been worked out for optical realization of complete heterophase balancing of carbon isotopes in various silicate materials (see Table I).

The carbon thresholds of detection have been estimated following the 3S-criterion proceeding from the blank signals variations (see Table I). Reproducibility of determinations is characterized by the relative standard deviation value equal to ab. 0.05-0.20 in the range of carbon concentrations of ab. 10^{-4} to 10^{-5} % mass.

Correctness of carbon detection has been checked by various methods, such as:

- varying the balancing conditions (weight quantities mass, balancing temperature and duration, dispersion of specimen particles, gas phase pressure in the exchanger). This method was applied for detecting carbon in various specimens with C concentrations from ab. 10^{-2} % to ab. 10^{-6} % mass;

- synthetic specimens analysis on the basis of pure

Table I

Conditions of carrying out heterophase isotopic balancing of C and their thresholds of detection

Element	Balancing temperature, °K	Balancing time, min	Mass of powdery specimen, g	C min, mass %
C	1500 - 1700	20	10	$1 \cdot 10^{-6}$
C	1300	240	10	$6 \cdot 10^{-5}$

SiO_2 with SiC admixtures (0.001%; 0.01 %; 0.1 %; 1 % mass.)

- analysis of synthetic specimens prepared of basis mineral fractions of granitoids with known content of both carbon and modelling in what concerns the composition the natural geological objects;

- comparing the results obtained in detecting carbon in silica with similar data obtained through the high-temperature extraction in vacuum.

The investigations performed have shown that the systematic error during carbon detection in silica and in granitoids is in all the cases considered rather small as compared with the random error which testifies to correctness of the results obtained when detecting carbon in silicate materials.

The isotopic-spectral method of detection of carbon

was used for investigation and perfection of the extra-clean quartz glass production technology; in geochemical researches on C distribution in ore-bearing massives and on establishing its (method) correlations in granitoids in connection with their metallogenetic features.

References

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