P296-WE

TOTAL SULFUR IN ROCKS AND KEROGENS AS A PART OF COMPLEX GEOCHEMICAL EXAMINATIONS - PRECISION AND VALIDATION STUDY

Veronika CULJAK[1], Marija MARICIC[1] and Darko SPANIC[1]

[1] *1INA – Oil Industry, Corporate Processe Function, Research and development Sector, Rock and Reservoir Fluid Research Laboratory Department, Geology and Geochemistry Section, 10002 Zagreb, Lovinciceva 1, Croatia*

Total sulfur in rocks, kerogens, oils and bitumens is a small but significant part of complex geochemical examinations. Determination of the total sulfur is, by definition, part of the ultimate analyses of rocks (cores and cuttings) serving a number of interests: combined with a major element analysis it amends the chemical composition useful in the process of petrologic determination of the rock mineral matrix. Total sulfur in oil is significant for physical and chemical characterization. Sulfur content classifies oils as high and low sulfur types.

Organic geochemical investigations include determination of the total sulfur content in a soluble organic matter (EOM) and in kerogen as well. Optical analyses of the organic matter determine primarily the type of kerogen and its maceral composition, but also a stage of thermal maturity. Organic petrologic examinations estimate the presence of pyrite in the organic matter but quantitative determination of sulfur confirms the results of optical analyses. Total sulfur content points to specific a kerogen structure. High percentage of sulfur in kerogen enables generation of hydrocarbons even in a diagenetic stage of thermal evolution as a result of the preferential cleavage at the weak sulfur linkages. Presence of pyrite suggests anoxic deposition environment conditions as well as presence of heavy metals which bond with sulfur in sulfides.

This work presents a test report, analytical precision and validation study of the sulfur determination on the coal and rock reference materials as well as the sulfur determination on the core, cutting and kerogen samples from Palmyra, Jihar, Al Bahra, Al Mahr and Mudawara exploration wells in Syria, referring the requirements of the standard test method ASTM D 4239-05 for conformity evaluation of the sulfur determination in Geochemical Laboratory:

ASTM D 4239-05 is the test method for sulfur in the analysis of coal and coke samples using high-temperature tube furnace combustion method, while our samples are mostly cores, cuttings and kerogens. Silicate rocks are inherently heterogeneous materials, since they are composed of discrete minerals of diverse chemical composition and physical character. The ultimate limitation of analytical precision is therefore the homogeneity of the

rock, as well as the complex nature of kerogen. That makes the sulfur analysis in rocks and kerogen a demanding analysis, according to the ASTM D 4239-05 standard test method requirements. Some of the uncertainties regarding the sample homogeneity effects are overcome by the rock crushing specified by ASTM D 4239-05. Those rock samples should be milled to pass completely a No 60 (250µm) mesh sieve or even a No100 (150µm). Good repeatability values are sometimes hard to obtain on the kerogens and rocks with a high content of sulfur. It seems that enlarged amount of vanadium pentoxide (0.8 to 1.0 g for approx. 0.50 g kerogen or rock sample), as combustion aid substance during analysis, improves results and repeatability values of the analysis.

Good accuracy and precision of the sulfur analysis in rocks and kerogens, using high-temperature tube furnace combustion method, are strongly based upon the analysis of the reliable, specific reference materials related to the nature and to the range of sulfur values of the materials to be tested. The accuracy requirement according to ASTM D 4239-05 test method for coal and coke can be achieved, under defined conditions, in the analysis sample of rocks and kerogen.

REFERENCES

Potts, P. J., 1995. A Handbook of Silicate Rock Analysis, Blackie Academic and Professional, an Imprint of Chapman & Hall, Glasgow 964, ZNZ, UK

Waples, W. D., 1985. Geochemistry in Petroleum Exploration. – D.Reidel Publishing Company, Dordrecht/Boston/Lancaster, USA,

EURACHEM/CITAC Guide, 2000. Quantifying Uncertainity in Analitical Measurement, Second Edition

ASTM D 4239 - 1995., Standard Test Methods for Sulfur in the Analysis Sample of Coal and Coke Using High-Temperature Tube Furnace Combustion methods

Barić, G. & Spanic, D., 1991. Application of optical methods in source rock determination (in Croation). – Geol. Vjesnik, 44, 313–320,Zagreb.

INA – Internal reports