

DIRECT AA MERCURY DETERMINATION IN OIL AND OIL PRODUCTS

Determination of mercury in oil and petroleum hydrocarbons is currently a vital problem due to the fact that the regulations for the mercury content in emissions from thermal power plants are becoming ever more stringent, and mercury poisons catalysts used in oil refining. Complex organic matrix of oil and low mercury content (average concentration does not exceed 30 $\mu\text{g}/\text{kg}$, the highest concentration being 20 000 $\mu\text{g}/\text{kg}$) make oil one of the most difficult objects for quantitative analysis for mercury.

Practically all the AA and AF methods of mercury determination in oil involve the stage of the oil decomposition with acids, which increases the detection limit and time of analysis, and gives rise to errors.

MEASURING METHOD

This method of mercury determination in crude oil and oil products is based on the atomization of mercury contained in the sample in a PYRO-915 attachment and subsequent mercury determination by flameless AAS in a mercury analyzer RA-915+. The mercury AAS analyzer RA-915+ with the Zeeman background correction equipped with a thermal decomposition attachment PYRO-915 allows determination of mercury in oil, food and other samples with organic matrix without sample preparation and mercury accumulation on a sorbent.

Mercury content in the sample is determined from the integrated analytical signal with due account of the preset calibration coefficient (from any reference mercury sample).

The two-section atomizer PYRO-915 consists of evaporator, in which evaporation of liquid samples and hydrolysis of solid samples are carried out, and of the heated reactor, in which catalytic destruction of the sample matrix compounds proceeds. After the pyrolyzer, the gas flow heated to 800 °C directly enters the cell of the analyzer with the Zeeman correction. The effect of the remaining impurity compounds is eliminated due to the high selectivity of the RA-915+ analyzer. Even if the optical density of the non-selective absorption is high (more than 2), no false signals appear, which allows a considerable increase of the sample weight (without accumulating mercury on the sorbent) and thereby lowering the concentration detection limit. The absence of cold ducts and smoke traps between the pyrolyzer and the cell makes it possible to avoid mercury sorption on them and thereby to improve the analysis reproducibility and correctness.

ANALYSIS FEATURES

- No sample preparation is necessary.
- Monitoring of the nonselective absorption during measurements makes it possible to effectively select the permissible weight of oil and petroleum hydrocarbons of any composition and thereby to avoid errors in the analysis.
- Mercury determination without its preliminary accumulation on a gold sorbent.
- There are no cold sections in the gas duct between the atomizer and analytical cell.
- Wide dynamic measurement range: 3 orders of magnitude without diluting the sample.
- The determination limit is 10 times lower than the average mercury content in oil sample.
- No need for cylinders with compressed oxygen or other gas.
- Visualization of the mercury release from the sample via a user-friendly computer interface.
- The calibration coefficient is preset from a reference mercury sample of any composition.



ANALYTICAL CHARACTERISTICS

Sample weight	up to 100 mg (oil) up to 50 mg (gasoline)
Detection limit	1–2 µg/kg (oil) 2–5 µg/kg (gasoline)
Measurement time	< 2 min
Air flow rate	1 l/min
Upper limit of the measurement range	10 000 µg/kg

The validity of the method is proved by the agreement between the measured and certified mercury concentrations in various reference samples with organic matrix (maximum discrepancy being less than 14%).

No	Reference sample code	Sample weight, mg	C, µg/kg	C _{CO} , µg/kg	Δ, %
1	Milk powder BCR-150	109	8.1	9.4±1.7	-14
2	Cow muscle BCR-184	29	2.3	2.6±0.6	-13
3	Coal NIST 1630a	60	95	105±23	-9
4	Shark liver DOLT-2	110	1960	2140±240	-8
5	Shark muscle DORM-1	100	820	798±74	+4

Comparison of the results of mercury determination in oil light fractions obtained using RA-915+ with the PYRO-915 attachment and by the neutron activation analysis (NAA)

No	C, µg/kg		Δ, %
	RA-915	NAA	
1	15	16	+6
2	21	25	-16
3	25	28	-11
4	28	22	+27

Results of mercury determination in crude oil in various oilfields

No	Uzen oilfield		Karazhe oilfield	
	Sample weight, mg	C, µg/kg	Sample weight, mg	C, µg/kg
1	70	4.1	40	670
2	80	5.5	52	770
3	87	5.5	37	630
4	80	6.4	35	690
5	90	6.4	34	700
6	98	6.4	28	710
	Average value 5.6 µg/kg SD 0.7 µg/kg RSD 12%		Average value 690 µg/kg SD 34 µg/kg RSD 5%	

Results of mercury determination in commercial gasoline

No	Sample weight, mg	C, $\mu\text{g}/\text{kg}$
1	14	74
2	20	78
3	18	77
4	17	71
5	22	69
6	20	85
		Average value 75.4 $\mu\text{g}/\text{kg}$ SD 6.7 $\mu\text{g}/\text{kg}$ RSD 8%

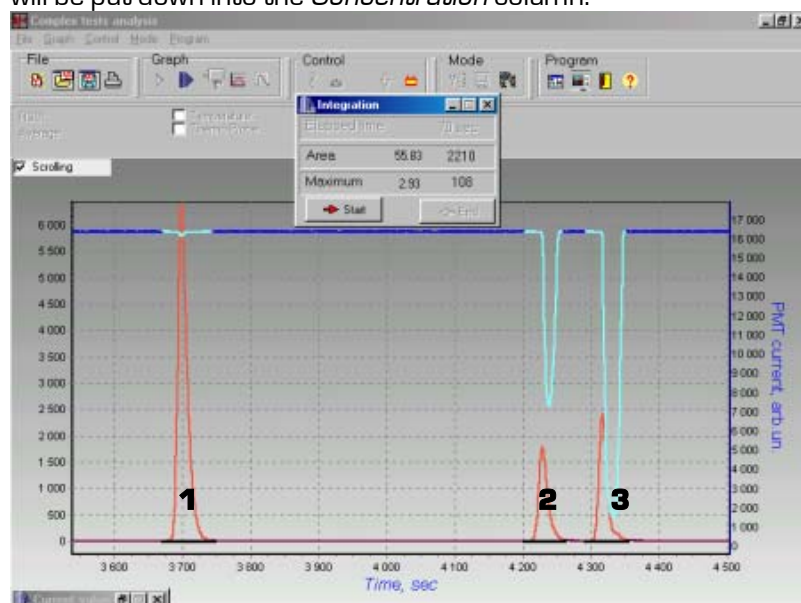
PROCEDURE OF OIL AND PETROLEUM HYDROCARBON ANALYSIS

Put the known amount of a sample in the injection spoon and write the sample weight in a proper entry in the program table.

Click button **Start** and immediately insert the spoon with the sample into the atomizer.

Upon completion of the atomization process (for about 40–100 s), click button **End**. The analytical signal will be automatically written in the table.

To calculate the results, click button **Calculation** on the tool bar. The analytical signal will be evaluated in the concentration units in accordance with the last calibration. Calculation result will be put down into the *Concentration* column.



A screenshot for the case of mercury determination in crude oil at the Karazhe oilfield.

- 1** – reference sample SORT 1 (1000 $\mu\text{g}/\text{kg}$), sample weight 87 mg;
- 2** – oil: 40 mg (measured value is 670 $\mu\text{g}/\text{kg}$)
- 3** – oil: 52 mg (measured value is 770 $\mu\text{g}/\text{kg}$)

This is a graph, which a user sees on the screen of a monitor during measurement. The red line is the analytical signal, and its enveloped area is proportional to the mercury weight in the sample. The blue line is the signal of the background absorption. The first peak is the signal from a reference sample (1000 $\mu\text{g}/\text{kg}$, sample weight 87 mg), used for calibration. The second and third peaks are signals from oil samples of different weights, 40 and 52 mg (Karazhe oilfield). It can be seen that it takes only 50–70 s to determine mercury content in the sample. The measured mercury concentrations in the sample were 670 and 770 $\mu\text{g}/\text{kg}$.