

THE INVESTIGATION OF GASOLINES AND MINERAL OILS BY X-RAY FLUORESCENCE SPECTROGRAPHY

THE DETERMINATION OF THE LEAD CONTENT OF ETHYLGASOLINES AND
THE INVESTIGATION OF TRACE ELEMENTS IN MINERAL OILS

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For the investigation of the application possibilities of X-ray fluorescence spectrography, gasoline samples with a known content of tetraethyl lead were used.

The determination of lead in gasolines is made by X-ray fluorescence spectrography, according to the principle of comparison. For the analysis, a standard of known content is necessary in order to make the comparison as related to this. In the course of the analysis, the intensity of the lines of the gasoline under investigation, respectively that of the standard lead are measured, and the lead content read off from the standard diagram previously prepared, at a point corresponding to the ratio of the two intensities.

For the construction of the standard diagram, different gasolines with known quantities of tetraethyl content are needed. The lead concentration of the gasolines containing tetraethyl lead changes after a longer period on account of the evaporation of the gasoline, and the tetraethyl lead will disintegrate when exposed to X-rays. Therefore gasolines containing tetraethyl lead cannot be used as reference standards.

The composition of a metal sample does not change under the influence of X-rays; it does not diminish or suffer any alterations, therefore the intensity of the lead line will remain constant.

Prior to the construction of the standard diagram one must be ascertained whether the absorption conditions of the gasolines originating from different places are identical, and what influence the eventual trace elements contained exert upon the determination of lead.

Gasoline contains a single heavy element; that is lead. The others are of low, respectively medium atomic weight; thus the intensity of lead radiation depends solely upon the lead concentration. No matrix effect is made on it by its environment.

According to PREIS, ESENWEIN [1] the determination of lead in gasolines is mostly disturbed by bromine. In order to study the effect of bromine 0.5, 1.0, 1.5, 2.0, 2.5 ml TEL/litre (tetraethyl lead = TEL) were added to gasolines distilled from crude oils taken from six different fields.

The crude oils originated from the following fields: 1. Lispe. — 2. Mezőkeresztes. — 3. Biharnagybajom. — 4. Hahót. — 5. Battonya. — 6. Demjén.

It was established that no considerable difference exists, between the bromine contents of the gasolines originating from the six different deposits but having the same content of tetraethyl lead.



Fig. 1. The Br $K\alpha$ lines of gasolines with a content of 2.5 ml TEL/litre, originating from the six fields

The bromine gets into the gasoline together with the tetraethyl lead.

The maxima of Fig. 2, marked by 1, 2, 3, show the Br-intensity diagrams of gasolines with contents of 0.5, 1.5 and 2.5 ml TEL/litre.

Departing from identical ethyl fluids, the bromine content at a certain given mixing ratio of tetraethyl lead and gasoline is always the same, therefore the bromine has no matrix effect on the intensity of lead radiation.

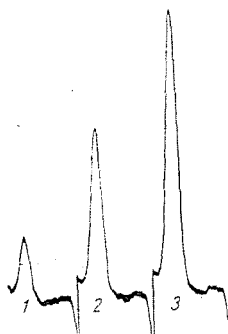


Fig. 2. The Br $K\alpha$ lines of gasolines with contents of 0.5, 1.5 and 2.5 ml TEL/litre

Similarly no matrix effects are produced in the determination of lead by gasolines from different origins or with contaminating elements either.

The decomposition of tetraethyl lead falsifies the determination of lead. Therefore, we examined the length of the period of time after which the decomposition of tetraethyl lead sets in under the effect of X-ray radiation. According to our results, decomposition set in after about 15 minutes.

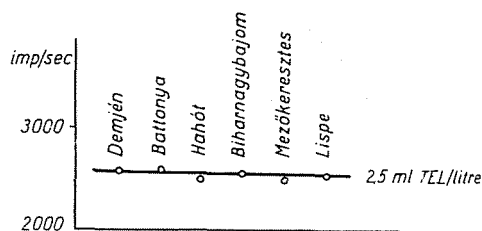


Fig. 3. The lead intensity diagram of gasolines with a content of 2.5 ml TEL/litre, originating from the six fields

During the determination of lead, the gasoline is exposed to X-radiation for a period of 64 seconds. Within this period no decomposition follows, consequently this does not disturb the measurement of lead intensity.

It has been shown by our investigations up to the present, that the lead content of gasolines distilled from six different crude oils can be determined from a single diagram.

For the construction of the standard diagram, gasolines of following tetraethyl contents were used: 0.1, 0.5, 1.0, 1.5, 2.0 and 2.5 ml TEL/litre.

The following ratio serves for the indication of lead intensity:

$$I = \frac{I_{\text{Pbpr}} - I_{\text{prbase}}}{I_{\text{Pbet}} - I_{\text{etbase}}} \quad (1)$$

I_{Pbpr} = intensity measured in gasoline on the lead line,

I_{prbase} = basic intensity of the gasoline,

I_{Pbet} = intensity measured on the lead line of the metal standard,

I_{etbase} = basic intensity of the metal standard.

The evaluation standard diagram can be seen in Fig. 4. The sample-container is a plexiglas cuvette having a 29 mm inner diameter and a wall thickness of 1 mm, with a bottom part of milard foil. The gasoline to be investigated is poured into this container, and the latter is placed in a metal sample-holder of 31 mm inner diameter.

The measurements were made with a Müller-Mikro 111 X-ray spectrograph.

Examination conditions: gold tube, 50 kV, 20 mA, topaz analysator crystal, 64 x, 32 sec. $\text{PbLa } 2\theta = 51.35^\circ$; the base was measured in Pb-free

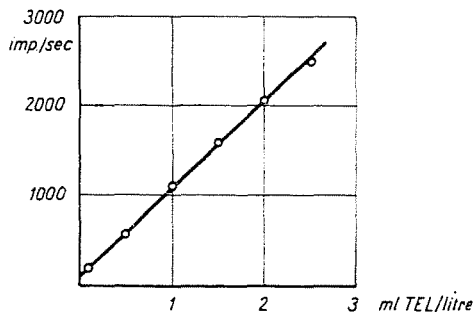


Fig. 4. Standard diagram for the evaluation of lead in the function of intensity — ml TEL/litre

gasoline discriminator: channel height 28 V, breadth 8 V, intensity 4, scintillation 840 V.

The dispersion was computed from 74 measurements. The measurements were made by different persons on different days.

Dispersion range: $\pm t_{(N)} \cdot S_{(N)}$,

$$\text{where } S_{(n)} = \sqrt{\frac{\sum_{i=1}^N \delta^2}{N - g}} \quad (2)$$

δ = deviation of the individual measurements from the average,

N = number of measurements = 75,

g = number of measurement groups = 25,

$t_{(N)}$ = at a security of 95% = 2.02

to 10 imp/sec, 0.01 ml TEL/litre correspond.

$\sigma = \pm t_{(N)} \cdot S_{(N)} = \pm 2.02 \cdot 31 = \pm 62 \text{ imp/sec} \cdot \pm 0.06 \text{ ml TEL/litre}$.

If the measuring period is taken for 64 seconds, the dispersion range decreases to half its value.

The followings were established:

1. With the Müller-Mikro 111 X-ray spectrograph, by the procedure known from literature, the lead can be determined from gasoline.

2. Analyzation period: 3–4 minutes.

3. With an increase of the measuring period the dispersion does not exceed MSz specifications.

4. The lead content of gasolines distilled from crude oils from six different deposits in Hungary, could be determined with a single diagram.

The influence of n.heptane, benzene, toluene, benzene + toluene (50–50%) on the determination of tetraethyl lead

We investigated the question, what influence n.heptane, benzene, toluene, benzene + toluene (50–50%) have on the intensity of the $K\alpha$ line of lead.

The investigations were made under the same conditions as the previous ones. For our measurements we used n.heptane, benzene, toluene, benzene + toluene (50–50%) pure and with 0.5, 1.0, 1.5, 2.0, 2.5 ml TEL/litre content.

The intensity of the Pb $K\alpha$ lines of these samples was measured. The intensity (in imp/sec) as a function of tetraethyl lead content can be seen in Fig. 5.

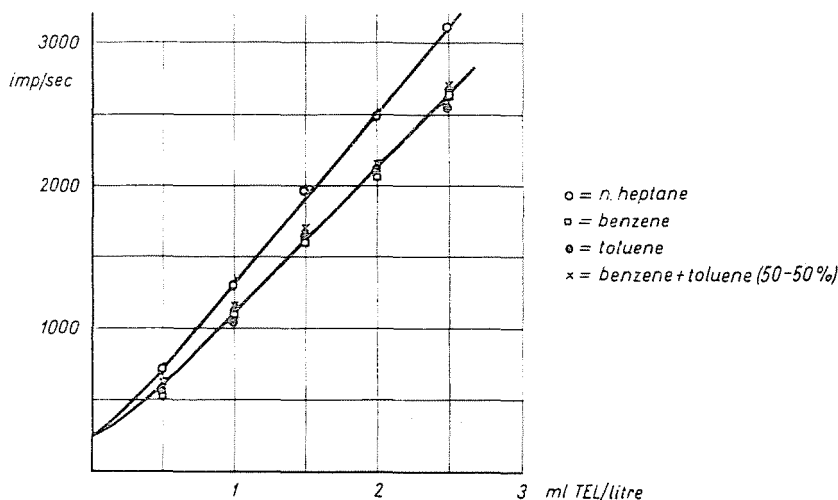


Fig. 5. The influence of various types of hydrocarbons upon the determination of the lead content

Symbols:

- = n.heptane
- = benzene
- = toluene
- × = benzene + toluene (50–50%)

According to Fig. 5, benzene and toluene, resp. their mixture diminish the intensity of the $K\alpha$ line of lead to the same measure.

This fact calls to the perceptible influence of the different types of hydrocarbons the attention, composing the gasolines, upon the determination of lead, further to the necessity of taking their influence into consideration. The examination of the distillation samples of the Petroleum Industrial Company of Komárom, made from Soviet crude oils proved the facts illustrated in Fig. 6.

b) Investigation of trace elements in Hungarian crude oils.

Our investigations related to the determination of trace elements of

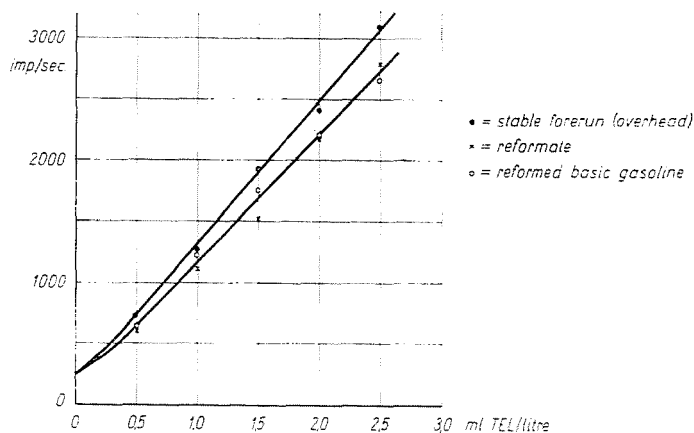


Fig. 6. The influence of various types of hydrocarbons of the mineral oil distillates upon the determination of the lead content (samples of the Petroleum Industrial Company of Komárom)

Symbols:

- ▲ stable forerun (overhead)
- × reformate
- reformed basic gasoline

crude oils were informative measurements limited to a qualitative determination of metallic components.

The mineral oils investigated came from the following fields:

Mark	Deposit
1	Battonya
2	Biharnagybajom
3	Demjén
4	Hahót
5	Kardoskút
6	Lispe
7	Mezőkeresztes
8	Nagylengyel
9	Szolnok

The crude oils were examined in a cuvette having a milard foil bottom part. The intensity diagrams of all the nine oils were recorded with a scintillation counter from 10° to 90° . The diagrams obtained showed nothing except the lines of scattered radiation from the gold tube.

When recording the intensity diagrams of the oils with a proportional counter, besides the gold lines also the $K\alpha$ intensity lines of Fe, Ni, V, Cu and Mn appeared.

The intensity diagram of oil No. 8, from 40° to 90° , can be seen in Fig. 7.

The Fe, Ni, V, Cu, Mn intensity diagrams of each oil sample were also recorded juxtaposed.

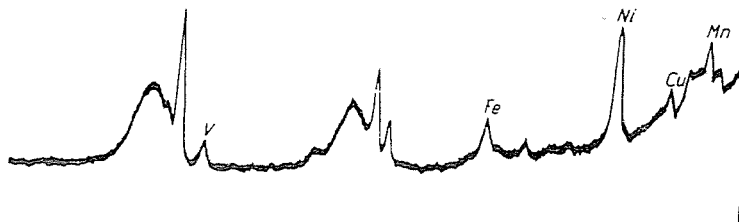


Fig. 7. The intensity diagram of the crude oil sample No. 8

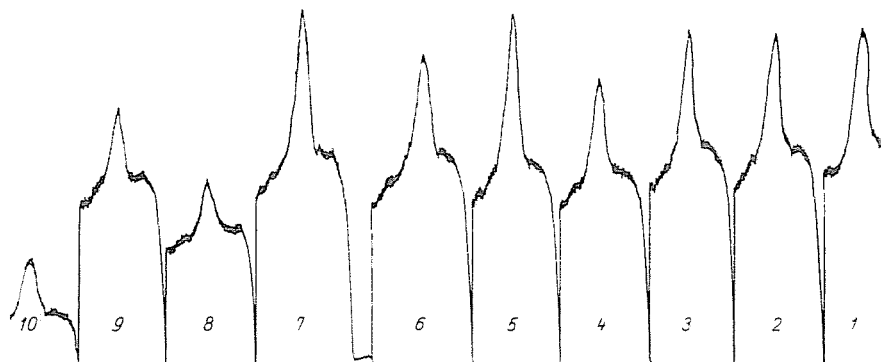


Fig. 8. The Fe K α intensity diagram of crude oil samples

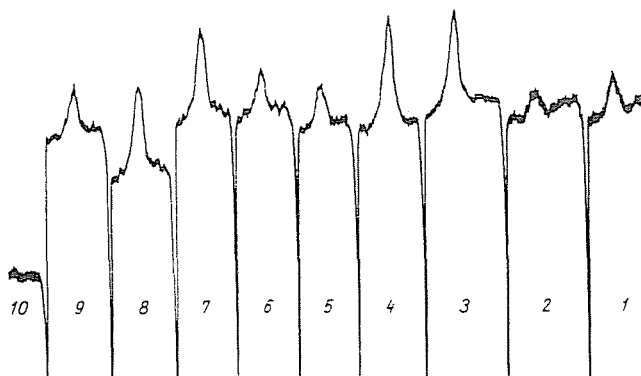


Fig. 9. The Ni K α intensity diagram of crude oil samples

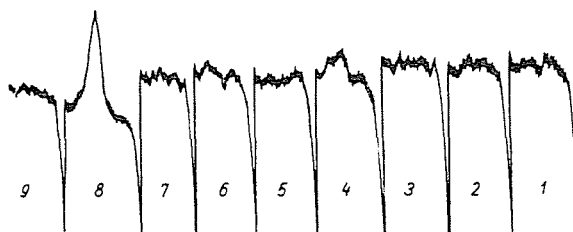


Fig. 10. The V K α intensity diagram of crude oil samples

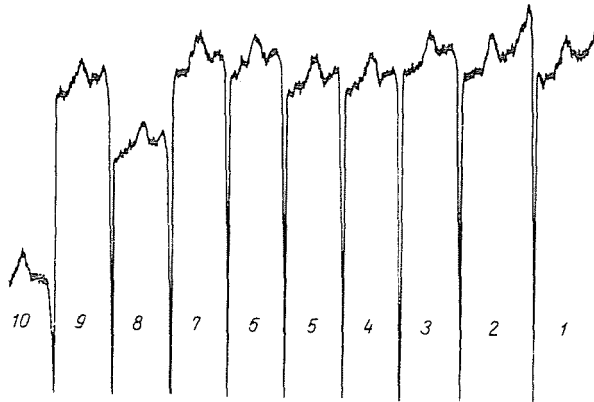


Fig. 11. The Cu $K\alpha$ intensity diagram of crude oil samples

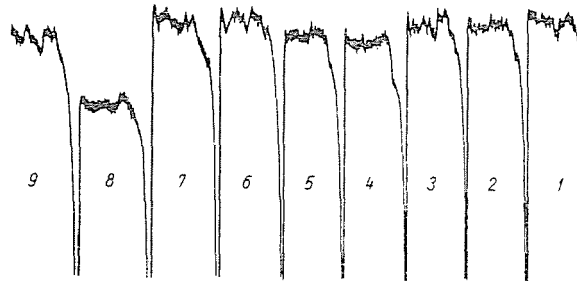


Fig. 12. The Mn $K\alpha$ intensity diagram of crude oil samples

Some of the diagrams contain also an intensity line No. 10. This was recorded from a sample with an Al content of 99.99% in order to establish, which part of the intensity originates from the contamination of the X-ray tube.

Examination conditions:

Diagram	kV	mA	Cry-tal	Attenuation rate	Time constant	Counter
7	50	20	LiF	32x	4	prop.
8	50	20	LiF	16x	4	prop.
9	50	20	LiF	64x	4	prop.
10	50	20	LiF	8x	4	prop.
11	50	20	LiF	8x	4	prop.
12	50	20	LiF	8x	4	prop.

A quantitative analysis of the qualitatively determined metal components accompanying the mineral oils investigated can be made by using appropriate standards.

The investigations were carried out in the Central Material Testing Laboratory of the Iron and Metal Works of Csepel, with the collaboration of the certificated physicists S. Szeimann and Sz. Szentpétery.

Summary

The lead content of ethylgasolines distilled from crude oils originating from different fields was investigated by X-ray fluorescence spectrography, then the influence of the individual types of hydrocarbons on these investigations determined. The contaminating trace elements of some Hungarian mineral oils were examined in a qualitative way.

Literature

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