# GLC and HPLC method for direct determination of the content of phenol and free alkylphenols in the polymer additives of the type of phosphoric acid aryl esters

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The paper presents a new approach to the direct determination of the content of phenol and individual isomers of isopropylphenol in technical and formulated products of additives to polymers on the base of the aryl esters of phosphoric acid, which is based on the gas-liquid (GLC) and/or high--performance liquid (HPLC) chromatographic method, respectively. The lower limit of detection of individual components is in the range of 0.005—0.01 %. The 95 % confidence limit is $(0.100 \pm 0.005)$ %. The methods were verified with some technical and formulated products of different provenience. The results of GLC and HPLC analyses were in good agreement. For comparison, the result obtained by spectrophotometric method is given for each sample.

В работе приводится описание метода прямого определения содержания фенола и отдельных изомеров изопропилфенола в продуктах и конечных добавках к полимерам на основе соответствующих ароматических эфиров фосфорной кислоты с помощью газовой хроматографии (GLC) и высокоэффективной жидкостной хроматографии (HPLC). Минимальная определяемая доля по массе отдельных компонентов колеблется от 0,005 до 0,01 %. Интервал надежности для 95 % уровня правдоподобности составляет $(0{,}100 \pm 0{,}005)$ %. Метод был проверен на нескольких продуктах и продажных добавках различного происхождения. Результаты анализов методами GLC и HPLC хорошо согласуются между собой. Для сравнения для каждого образца приведен результат спектрофотометрического анализа.

Substances of the type of aryl esters of phosphoric acid have as polymer additives been in use for several decades. They are used as plastifiers as well as flame retardants especially for production of plastics with special application lines

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(production of transport bands, conveyor belts for mines, production of plastics for motor-car industry and aviation industry, *etc.*). Owing to technological processes, the additives always contain variable amount of free phenolic compounds (according to the type of product). The analytical control of the content of free phenolic substances in polymers and in technological waste from their production has become in recent years a subject of increased interest of analytical chemists [1—10]. From the aspect of the use of an additive, which with 40—60 % represents in polymer one of its main components as well as regarding the well-known physicochemical and environmental properties of phenolic compounds there is an urgent need for a reliable knowledge of the content and/or composition of free phenolic compounds in corresponding additives even at the concentration level under 0.1 %. In available literature, however, no methods have yet been published allowing such analytical control. The content of free phenolic substances is in laboratory practice usually determined by nonspecific methods mainly based on extraction of the additive sample followed by spectrophotometric determination [11].

Two simple and plausibly reliable procedures for direct determination of the content of free alkylphenols and phenol in additives of the Retar type are described in this paper. The methods are based on GLC and/or HPLC determination. These procedures were verified with real samples of different origin.

## Experimental

### *Gas chromatography*

A Fractovap 4200 (C. Erba, Milan) gas chromatograph with a computing integrator Autolab IVB (Spectra-Physics, USA) was used. The separation was performed on a 300 cm × 2 mm ID glass column packed with 5 % OV-17 on Chromosorb G, 250/177 μm. The temperatures of the oven, injection part, and detector (FID) were 165 °C, 200 °C, and 250 °C, respectively. Nitrogen was used as carrier ($p = 0.18$ MPa). Individual standards of alkylphenols and phenol were prepared in the Research Institute of Chemical Technology, Bratislava. The samples of additives of Retar type were commercial products or laboratory samples incidentally selected. All the solvents used were of anal. grade purity. The content of individual components of interest in sample was determined by external standard method, *i.e.* comparing the peak area in sample chromatogram with the area of corresponding peak in the standard mixture, which contained 50 mg of each standard in 25 $cm^3$ of acetone. The solutions of samples were prepared by weighing 0.5 g of sample into a 25 $cm^3$ volumetric flask and filling with acetone up to the mark. The 2 $mm^3$ portions of the sample as well as of standard solution were injected onto the column with a 10 $mm^3$ Hamilton microsyringe.

### *Liquid chromatography*

A Varian 8500 liquid chromatograph equipped with a Variscan 635 UV VIS detector and a Varian, model 485, computing integrator, was used. We applied a 300 mm × 3.2 mm ID CGC column packed with Separon SIX C-18 5 μm (Laboratorní přístroje, Prague). Over potassium permanganate redistilled water was used in mobile phase. Mobile phase $V$(acetonitrile) : $V(H_2O) = 65:35$ with subsequent washing of the column with acetonitrile alone was applied to the column. The peaks were detected and integrated at $\lambda = 280$ nm. Sample solutions were prepared by weighing 5.0 g of sample into 10 $cm^3$ volumetric flask and diluting with acetonitrile up to the mark. The standard solution contained 10 mg of each standard in 10 $cm^3$ of acetonitrile. Content of individual compounds was quantified as in GLC method. Anal. grade acetonitrile was purified by additional azeotropic distillation and rectification before use. The 5 $mm^3$ portions of standard and sample solutions were applied onto the column.

### *Spectrophotometric method*

500 mg of sample was dissolved in 25 $cm^3$ of $CCl_4$. The solution was extracted with aqueous solution of KOH ($c$(KOH) = 0.1 mol $dm^{-3}$). The summary content of phenolic substances was determined by measuring the absorbance of the KOH solution at $\lambda = 280$ nm and comparing with the absorbances of standard solutions of phenol in aqueous KOH (calibration curve technique).

## Results and discussion

Table 1 gives the results of determination of the content of phenol and free phenolic compounds in Retar additives obtained by three different methods.

*Table 1*

Overall content of phenolic substances in samples

| Sample | Summary mass fraction/% | | |
|---|---|---|---|
| | GLC | HPLC | Spectr. |
| *6* | 0.74 | 0.76 | 0.60 |
| *8* | 0.84 | 0.83 | 0.74 |
| *10* | 2.66 | 2.64 | 2.22 |
| 6AN | 1.33 | 1.34 | 2.01 |
| Pliabrac | 0.05 | 0.05 | 0.03 |
| Reofos | 0.03 | 0.03 | 0.03 |
| Retar (USSR) | 0.08 | 0.08 | 0.10 |
| Retar 131 | 0.01 | ND | 0.12 |

ND — nondetermined.

Samples *6*, *8*, *10*, and 6AN were laboratory prepared additives, whereas all other samples were commercial products. The results give clear evidence of a good agreement between GLC and HPLC methods. At the low concentration the results of spectrophotometric determination are rather consistent with GLC and/or HPLC figures. However, considerable differences appear for the samples with higher content of phenolic substances, which is due to the different values of the molar absorptivities of individual compounds. Moreover, if the product contains mono- and diarylphosphoric acids, further impairment of the results arises, which is documented by sample Retar 131.

The HPLC separation of isopropylphenols of interest was carried out with the 250 mm × 2.2 mm ID Micro-Pack CH-10 (Varian) and 300 mm × 3.2 mm ID

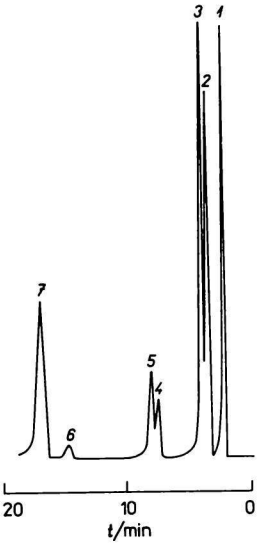


*Fig. 1.* HPLC chromatogram of a mixture of standards.
Peak order: *1.* phenol;
*2.* 4-isopropylphenol;
*3.* 2-isopropylphenol;
*4.* 2,4(2,5)-diisopropylphenol;
*5.* 2,6-diisopropylphenol;
*6.*2,4,5-triisopropylphenol;
*7.* 2,4,6-triisopropylphenol.

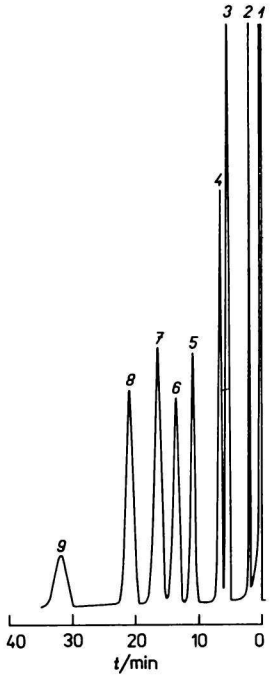


*Fig. 2.* GLC chromatogram of a mixture of standards.
Peak order: *1.* solvent;
*2.* phenol;
*3.* 2-isopropylphenol;
*4.* 4-isopropylphenol;
*5.* 2,6-diisopropylphenol;
*6.* 2,4-diisopropylphenol;
*7.* 2,5-diisopropylphenol;
*8.* 2,4,6-triisopropylphenol;
*9.* 2,4,5-triisopropylphenol.

Separon SIX C-18 columns, respectively. The peaks of 2,4-, 2,5-, and 2,6-diisopropylphenol overlapped on the Micro-Pack column. However, the column separates perfectly the possibly present mono- and diarylphospohric acids from phenol. On the Separon SIX C-18 column there is no overlapping of 2,4- and 2,6-diisopropylphenols. Only 2,4- and 2,5-diisopropylphenols overlap (Fig. 1). With respect to the technological processes there is but only theoretical possibility of presence of 2,5-diisopropylphenol in the samples. The drawback of the Separon column is in insufficient separation of the peaks of mono- and diarylphosphoric acids from the peak of phenol, which may, to a certain extent, impair the final result at very low phenol concentrations (under 0.1 %). The optimum separation conditions were found in NP-HPLC version using 250 mm × 6.1 mm ID Separon SI VSK 10 μm column. This column, however, does not fit the practical use because of overlapping of the peaks of the product (aryl phosphates) with the peaks of alkylphenols.

Under the conditions of GLC determination as described in Experimental, there is a perfect separation of all the compounds of interest on the column (Fig. 2). Mono- and diarylphosphoric acids as well as triaryl phosphates are not eluted from the column under the conditions given. Owing to these aspects GLC method appears to be superior to the HPLC. The possible decomposition of aryl phosphates in the injection part of the chromatograph, involving further release of phenolic compounds in the column was not observed. The substances condense in the void injection part of the column and do not interfere with GLC determination. They may be removed by mechanical cleaning approximately after 25 sample injections. In general the methods of HPLC and GLC may be considered to be equivalent. The presented experimental data reveal considerable unreliability of the results obtained by nonspecific spectrophotometric method comparing with HPLC and/or GLC results. Furthermore, HPLC and GLC methods represent substantial simplification and acceleration of the process of analytical control. The methods may also be considered as a positive contribution from the aspect of providing with unambiguous information on complete composition of the input raw materials in the production of plastics. Such requirements have economic as well as environmental background.

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