Determination of phenol in phenol tars from the cumene-to-phenol process streams with ^{13}C-NMR spectroscopy

The Analyst

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^{13}C-NMR spectroscopy has been employed for the determination of phenol in phenol tars originating from the process of phenol industrial synthesis. Relaxation times T_1 of ^{13}C nuclei in phenol and in dioxane (used as a standard for quantitation) have been measured in order to establish appropriate conditions for the acquisition of quantitative spectra. The results of ^{13}C-NMR analyses are compared with the results obtained with ^{1}H-NMR, infrared spectroscopy, ultraviolet spectroscopy, gas chromatography and bromometric titration. The accuracy and repeatability of the determinations have been tested on samples with added weighed amounts of phenol. A great advantage of the ^{13}C-NMR method is that three results from each spectrum are obtained, which may be averaged, while those involving large errors can be rejected. The scatter of the relative errors for single results has been tested and evaluated at the level ±0.8%.

There are perhaps three reasons why ^{13}C-NMR spectroscopy has commonly been considered to be unsuitable for chemical quantitative analysis. The first seems to be due to the problem of the acquisition parameters that must be fixed for the analysed system and used to avoid (or to reduce) the error resulting from the incompletely suppressed nuclear Overhauser effect (NOE) and from a slow longitudinal relaxation process; this error affects the accuracy of the determination. The long-lasting accumulation of a quantitative spectrum is another reason; it is equivalent to the comparatively small level of detectability of ^{13}C-NMR and results from both the long pulse repetition delays which have to be used and the low natural abundance of ^{13}C nuclei. Finally, the personal factor in quantitative NMR spectroscopy seems to be of importance; it manifests itself during the phase correction of a transformed spectrum and of integral curves, and is probably responsible for the general belief regarding the poor repeatability and low precision of NMR analyses. However, when quantitative NMR is properly used, it can be a very helpful tool in solving numerous chemical problems.

Phenol tar is a by-product of the cumene-to-phenol process (the cumene process); it is also the largest by-product stream in the whole phenol plant. Phenol tar is the most difficult stream to analyse. Most of the minor products find their 'last resting place' in the phenol tar, so that its qualitative composition is exceptionally rich, while the contents of particular compounds may vary within a wide range. The presence of phenol in the tar represents the direct loss in the process, and the operating conditions of the plant should be adjusted so as to maintain it at the lowest possible level. It usually varies within the range of 2% to 15%, but may be much higher when the plant operation is disturbed.

Three phenol tar samples analysed in this study, denoted as tar 1, tar 2 and tar 3, were taken at random directly from the process run at the Petrochemia S.A. Plants, Płock, Poland. The samples differ greatly in their quantitative composition, mainly with regard to the content of phenol itself, which varies from below 3% in tar 1 and tar 2 to over 40% in tar 3.

Experimental

^{13}C-NMR (25 MHz) inverse gated proton-decoupled (INVGATE) spectra were obtained with a Bruker (Rheinstetten, Germany) WP-100SY spectrometer at room temperature. The $\pi/2$ (90°) pulses were applied, with an acquisition time of 2.9 s. Time domain, 32K data points; free induction decay (FID) curves were exponentially multiplied (line broadening factor, LB = 0–0.5 Hz) and transformed at either 64K or 128K. The tar samples were analysed undissolved; a drop of deuterated cyclohexane was added to each sample as a lock. As an internal chemical shift standard, tetramethylsilane (TMS) was used. Longitudinal relaxation times were measured at 25 °C with the inversion–recovery pulse sequence (π–τ–$\pi/2$–FID) with proton-decoupling frequency on during the $\pi/2$ pulse and FID acquisition only. All analysed samples were sealed in tubes of 5 mm in diameter.

The purity of phenol added to the samples was of spectroscopic grade. 1,4-Dioxane (*p.a.*), used as a standard for quantitation, was rectified and the fraction 100.99–101.04 °C was retained and kept over molecular sieve (4 Å).

Results and discussion

The INVGATE ^{13}C-NMR spectra (aromatic ranges) of tars 3 and 1 are shown in Figs. 1 and 2, respectively. The signals of phenol are marked and assigned to carbon atoms in the molecule.

In NMR practice, it is usually assumed that, for quantitative purposes, a distance of at least $5T_1$ between subsequent $\pi/2$ rf pulses should be maintained; however, numerous authors suggest much longer delays.[1–3] Gillet and Delpuech[4] analysed the problem from a physical point of view and suggested delays of $6.5T_1$ if $T_1 < 30$ s and of $4.6T_1$ if $T_1 \geq 30$ s. However, it should be stressed that, if the T_1 values for an unknown and for a standard are close to each other, the delay may be significantly shortened.

The longitudinal relaxation times of the ^{13}C nuclei of phenol and dioxane in the analysed samples are presented in Table 1. The longest relaxation time in all the systems examined is for the C1 carbon atom in phenol, and the respective signal has been excluded from the analysis. The next longest T_{1C} value is that of dioxane; in tar 3, it was measured as 3.70 s, and so a delay of 5 × 3.70 s = 18.5 s was applied during the accumulation of the spectrum of tar 3. The relaxation in samples of tars 1 and 2 is much faster (T_1 < acquisition time = 2.9 s) and, for the

complete elimination of NOE, a delay of 6 × 2.9 s = 17.5 s must be applied. Each of the three phenol signals at δ 115.9, 130.0 and 120.5 ppm, corresponding to atoms C2, C3 and C4, respectively, was used for an individual determination. They were plotted together with the signal of dioxane (δ = 67.14 ppm) at the same scale on an A3 sheet of paper, and their field areas (Lorentzian lines) were approximated for the calculations by the field areas of triangles, or by the products of their heights and half-widths. This procedure is much more precise than the use of an integrator; it also significantly reduces the error due to overlapping of other signals (impurities).[5] The results of the analyses are listed in Table 2 and compared with the results of ^{1}H-NMR (only in tar 3, with 'internal normalization' to 100%, so the result is expected to be slightly overestimated), gas chromatography (OV-17/FAP 60/40 column, WHP-120 mesh), IR spectroscopy (the band at 510 cm^{-1}, originating from the out-of-plane ring deformation vibrations, according to the procedure described by Górska and Gluzińska[6]), UV spectroscopy (the band maximum at about 280 nm, after extraction of phenol with hot water, as described by Łabudzińska *et al.*[7]) and bromometric titration (extraction of phenol with hot water, bromination with an excess of potassium bromate and potassium bromide water solution, reaction of excess bromine with potassium iodide to obtain iodine and potassium bromide, and back-titration of iodine with sodium thiosulfate, according to a company standard utilized at Petrochemia S.A.).

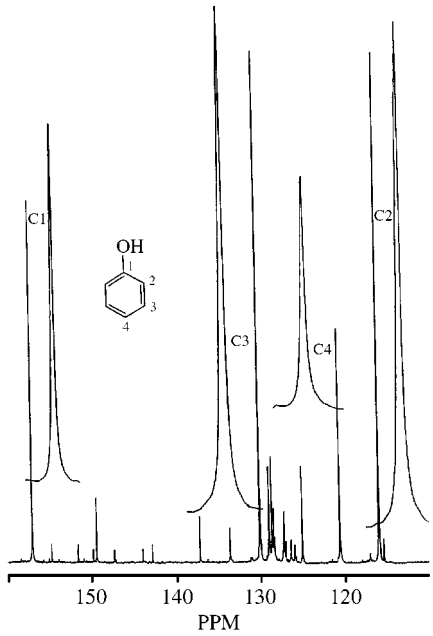

Fig. 1 Quantitative ^{13}C-NMR spectrum of tar 3 (over 40% phenol).

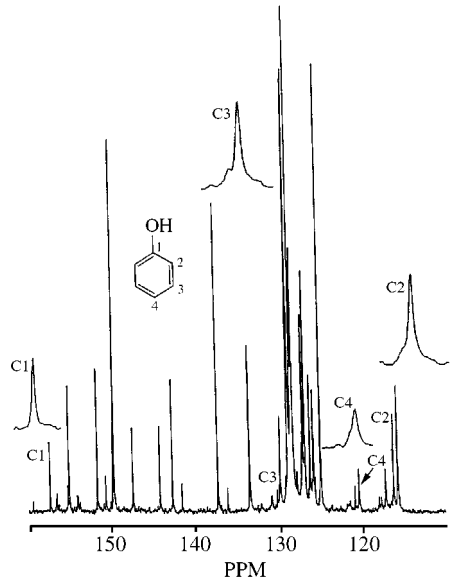

Fig. 2 Quantitative ^{13}C-NMR spectrum of tar 1 (about 2.5% phenol).

Most of these methods were also used for the analysis of samples of tars 1–3 after weighed amounts of phenol were added to each sample. The results are presented in Table 3. Pairs of results, placed in sections *a* and *b*, are presented for each sample. Section *a* represents the phenol percentages measured in the tar samples after the addition of phenol and recalculated for the original samples (without phenol added). These are supplementary results to those of Table 2, obtained by using the added amount of phenol as a kind of 'secondary standard'. The results in section *b* show the percentages of added phenol, calculated in order to verify the determination by comparison of the results before (*cf.* Table 2) and after the addition of phenol.

^{13}C-NMR seems to give the best results in this comparison; however, it should be emphasized that the determination of about 2% of phenol in a mixture with a spectrometer working at a ^{13}C frequency of 25 MHz is close to the limit of the possibilities of the method. IR spectroscopy is no more accurate (the band at 510 cm^{-1} is not completely isolated and its intensity changes slightly with small changes in the content of phenol), while the extraction of phenol with hot water is a critical stage in the accuracy (repeatability) of the determinations by both UV and titrimetric methods. One advantage of ^{13}C-NMR is that one spectrum provides three individual results (for signals of carbon atoms 2, 3 and 4); this allows the elimination of results involving large errors, while averaging of the individual results minimizes the error of the determination.

Table 1 Longitudinal relaxation times T_1 (in seconds) of ^{13}C nuclei of phenol and dioxane in samples of phenol tar (25 °C)

	T_{1C}/s (in phenol) at carbon atom				
Sample	C1 (C–OH)	C2	C3	C4	T_{1C}/s (in dioxane)
Tar 1	4.3	1.05	1.06	1.02	1.50
Tar 2	3.6	0.96	1.22	0.73	1.80
Tar 3	13.5	2.40	2.44	1.86	3.70

Table 2 Results of the determination (%) of phenol in three samples of phenol tar with ^{13}C-NMR, ^{1}H-NMR, IR spectroscopy, UV spectroscopy, gas chromatography (GC) and bromometric titration

	^{13}C-NMR								
Sample	C2	C3	C4	Average	^{1}H-NMR	GC	IR	UV	Titration
Tar 1	2.5	2.6		2.5	—	3.5	2.7	2.4	5.0
Tar 2	2.4	2.2	2.2	2.3	—	3.2	2.2	1.8	4.4
Tar 3	44.3	44.5	44.2	44.3	47.5	51.2	42.3	48.8	48.4

—, No determination was made; empty space means that the result was rejected.

Table 3 Results (%) of the analysis of samples with added amounts of phenol: *a*, determination of phenol, results recalculated for the original samples (*cf.* Table 2); *b*, determination of the added amounts of phenol

Sample + added phenol (%)		^{13}C-NMR				^{1}H-NMR	IR	UV	Titration
		C2	C3	C4	Average				
Tar 1 + 0.52%	*a*	2.7	2.7		2.7	—	2.8	2.7	
	b	0.71	0.63		0.67	—	0.62	0.78	
Tar 2 + 0.56%	*a*	2.3	2.2		2.3	—	2.9	1.9	
	b	0.59	0.51		0.55	—	1.30	0.68	
Tar 3 + 10.2%	*a*	43.9	44.2	44.2	44.1	48.4	48.7	59.8	49.5
	b	9.8	10.1	10.1	10.0	10.7	16.6	21.2	11.3

—, No determination was made; empty space means that the result was rejected.

The basic problem of analysing small quantities of substances with ^{13}C-NMR (particularly with quantitative ^{13}C-NMR) is the long-lasting accumulation of a spectrum; this can be overcome by using spectrometers working at the highest possible field strength; additionally, this makes it possible to take advantage of lower T_1 values.[8] The method may be recommended for the periodic verification of results obtained with other methods and for adjudicating analyses in cases of discrepancy. It can also be applied for the accurate and repeatable determination of phenol in numerous systems.

The following test was carried out to verify the performance of quantitative ^{13}C-NMR. The spectrum of tar 3 was accumulated three times, with a variable pulse repetition delay t_r of 5, 7 and 10 times the T_{1C} value for dioxane (equal to 3.70 s; *cf.* Table 1), *i.e.* 18.5 s, 25.9 s and 37.0 s, respectively. When the mean value of the three results obtained with t_r = 37.0 s for signals corresponding to C2, C3 and C4 atoms (according to the foregoing procedure) was assumed to be the real percentage of phenol in the tar, none of the absolute values of the relative errors of the nine (individual) results of the determination exceeded 0.8%. This means that the correct conditions for the accumulation of quantitative ^{13}C-NMR spectra were maintained in all cases. This also testifies to the high precision and good accuracy of the analyses. For comparison, the relative error of the determination with the C1 signal (T_1 = 13.5 s), for which the conditions for the accumulation of quantitative spectra were not maintained, varied from about −2% for t_r of 37.0 s (t_r/T_1 = 2.7) up to −12% for t_r of 18.5 s (t_r/T_1 = 1.4). It should also be mentioned that the dispersion of the errors in the results obtained with the signals corresponding to C2, C3 and C4 atoms increased five times (from ±0.8% to ±4.0%) when the heights of the integral curves were compared instead of the triangular field areas.

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