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Gas Chromatographic Determination of Aniline and Nitrobenzene in Ambient Air

by Jarosław Bartulewicz[a], Ewa Bartulewicz[a], Janusz Gawłowski[b] and Jan Niedzielski[b]

[a]*Laboratory of Environmental Chemistry, National Foundation for Environmental Protection, 02-089 Warsaw, Poland*
[b]*Department of Chemistry, University of Warsaw, 02-089 Warsaw, Poland*

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The method of nitrobenzene and aniline determination in ambient air is described. Nitrobenzene undergoes sorption on Chromosorb 102 while aniline is sorbed on Chromosorb G doped with 4% of orthophosphoric acid. In both cases desorption is carried out with benzene followed by capillary gas chromatographic analysis. Desorption of aniline occurs at alkaline pH. Limits of determination for nitrobenzene and aniline are 1 and 2 μg m^{-3}, respectively, if flame ionization detector is used. Electron capture detector enables to decrease the limit of nitrobenzene determination down to 0.1 μg m^{-3}.

Praca zawiera opis metody oznaczaniu nitrobenzenu i aniliny w powietrzu. Nitrobenzen jest adsorbowany na Chromosorbie 102, zaś anilina na Chromosorbie G z naniesionym kwasem ortofosforowym. Do desorpcji w obu przypadkach służy benzen, tyle że w przypadku aniliny desorpcja biegnie w środowisku zasadowym. Ostateczna analiza jest przeprowadzana techniką kapilarnej chromatografii gazowej. Granice oznaczalności nitrobenzenu i aniliny wynoszą odpowiednio 1 i 2 μg m^{-3}, jeśli używać detektora płomieniowo-jonizacyjnego. Użycie detektora wychwytu elektronów obniża dziesięciokrotnie granicę oznaczalności nitrobenzenu.

Aniline and nitrobenzene are the basic raw materials widely used in the polymer, rubber, agricultural and dye industries, mostly for the production of explosives, pesticides and polyurethane foam. It is estimated that nearly 1.5×10^9 kg of aniline and 1.0×10^9 kg of nitrobenzene are produced currently worldwide. It is of interest that about 300 chemical products are at present manufactured from aniline alone. However, both the chemicals are known poisons, listed as priority pollutants

by the U.S. Environmental Protection Agency [1], with acute and chronic effects. The inhalation and especially the ready absorption through the skin may lead to cyanosis with formation of methemoglobin, to anemia and liver damage [2,3].

The reports on aniline and nitrobenzene determination in air are not numerous, although explosives and related compounds have attracted considerable attention but mostly in munition plant wastewater rather than in air. As direct sampling is limited to larger concentrations, in order to reach low levels involved all methods rely upon a preconcentration stage in which a known volume of air is drawn through an adsorption tube. Desorption of compounds enriched on solid sorbents is done with liquids or thermally; polar as well as apolar solvents are used [4,5]. Although a variety of materials have been used, most often activated charcoal or silica gel become a sorbent of choice [6–8]. Silica gel was reported to perform very well for aniline [9]. Desorption with methanol yielded 96% recovery [10]. Charcoal adsorbs nitrobenzene very effectively. Desorption with toluene was reported to give 91% recovery, while with diethyl ether the recovery was 100% [11]. Also resin adsorption employing Porapack R, Porapack S, [12,13], Amberlite XAD-4 and Amberlite XAD-2, -4 and -8 (1:1:1) [14] was used for sample preconcentration. A newer technique involves the use of a porous polymer sorbent, followed by thermal desorption with cryofocussing into the gas chromatograph. Aniline and nitrobenzene were successfully sampled on Tenax TA (poly-2,6-diphenyl phenylene oxide) [15–17] and on Carbotrap [15] which is a very pure graphitized carbon black.

Most of the work was concerned with industrial workplace exposure [16–19] or with laboratory indoor air [20,21], with both active [16,17] and passive [22–26] approaches being examined. Determination of aniline specifically in ambient air has been described by Chinese workers [10,27], while that of aniline by Japanese authors [28].

While spectrophotometric determination of aniline has been described [29,30] and piezoelectric sensors can be useful for indoor determinations of both aniline and nitrobenzene [31–34], chromatographic methods predominate among analytical techniques. Gas chromatography can employ usual flame ionization detection [35,36] or more selective and sensitive electron capture [12,22,23,37,38], chemiluminescence [14,39] or nitrogen selective detection [40]. The use of mass spectrometer coupled with gas chromatograph for the determination of aniline [19] as well as the use of mass spectrometer alone employing resonance-enhanced multiphoton ionization for the determination of nitrobenzene [41] have been described. Alternatively high performance liquid chromatography can be used [10,13,42–45].

The objective of this work is to develop as convenient and cost-effective procedure of analysis as possible which could be adopted for routine monitoring. Based on our own experience and the survey of literature data we have opted for sorption followed by solvent desorption as a method of enrichment, to be followed by gas chromatographic determination using flame ionization detection for aniline, and flame ionization combined with electron capture detection for nitrobenzene.

EXPERIMENTAL

Chromatography

The HP 5890 (Hewlett–Packard) and the GC-14A (Shimadzu) gas chromatographs, both equipped with flame ionization detectors, computer acquisition and processing systems and split/splitless port units for capillary columns were used. The GC-14A featured additionally a constant current electron capture detection.

Two capillary columns were employed: HP-1, 5 m, 0.53 mm ID, film thickness 3.0 μm, obtained from Hewlett–Packard; and SPB-5, 15 m, 0.53 mm ID, film thickness 1.5 μm, obtained from Supelco.

Chemicals

Chromosorb 102 and Chromosorb G were obtained from Applied Science.

Analytical reagent grade nitrobenzene, aniline, 85% orthophosphoric acid and solvents (methylene chloride, benzene, butyl acetate, methyl alcohol) were purchased from PPCh Gliwice and used without further purification.

RESULTS AND DISCUSSION

Preliminary experiments

In preliminary experiments the efficiency of nitrobenzene and aniline adsorption on solid sorbents was fully confirmed. Both can be adsorbed quantitatively on activated charcoal from the volume of air exceeding 100 l. However, desorption from charcoal with pentane or benzene is poor, below 20%. Therefore Chromosorb 102 was selected for further experiments. Adsorption of 5 μg of nitrobenzene or aniline on 100 mg of Chromosorb 102 was followed by extraction with 1 ml of benzene. While 100% recovery of nitrobenzene was superb, that of aniline, 40–50%, was not. Apparently acidic active centres, such as phenolic or carboxylic groups, are present on the sorbent surface as a result of oxidation. An attempt to deactivate such centres with the use of 0.2 ml of 0.1 mol l^{-1} NaOH was abortive. The use of strong organic bases such as hydroxylamine and propanolamine resulted in some increase in aniline desorption but to a value not better than 60–70%. These efforts were discontinued. Instead, the use of an acid-coated sorbent, recommended for the sampling of low molecular weight aliphatic amines [46], was examined. Chromosorb G doped with 85% orthophosphoric acid, 4% by weight, was tested. Aniline was sorbed under static conditions, assisted with vigorous shaking. 100 mg of the acidic sorbent underwent successive elutions with 0.5 ml of 0.1 mol l^{-1} NaOH and 0.5 ml of benzene. The recovery of aniline increased up to 90%. Moreover, the adsorption was selective as only aniline, benzene and benzene contaminants peaks were present on chromatograms. Thus, Chromosorb 102 was selected to adsorb nitrobenzene while Chromosorb G coated with orthophosphoric acid was selected to adsorb aniline.

Adsorption efficiency

Nitrobenzene. Commercial samples of Chromosorb 102 were contaminated. While purification by heating in the stream of nitrogen for 4 h at a temperature of 200°C was not sufficient, multiple washings with benzene, followed by drying in a drier at a temperature of 60°C, were. Nitrobenzene peak was not threatened by any overlap after such a procedure.

The tubes were filled with two sections of Chromosorb 102, 50 mg each. 1.0 μl of nitrobenzene dissolved in methanol to make 1–10 mg ml^{-1} solution was introduced into the stream of air flowing at a rate of 100 l h^{-1}. The total volume of air passed through the tube was 100 l. Breakthrough has never been observed, nitrobenzene being found only in the first section of Chromosorb. Saturation of air with water vapour did not result in any deterioration of sorbent performance. Thus, both dry and humid air can be sampled for nitrobenzene using this method.

Aniline. The same procedure as that employed for nitrobenzene was used. 100 mg of Chromosorb G was coated with 4% by weight of orthophosphoric acid. Aniline was dissolved in methanol to make 0.6–10 mg ml^{-1} solution. 100% adsorption from 100 l of both dry and humid air has always been observed.

Recovery

Static adsorption of nitrobenzene. To 50 mg of 60/80 mesh Chromosorb 102 placed in a 3-ml test tube, 1 μl of 3 mg ml^{-1} solution of nitrobenzene in methanol was added. The test tubes were capped with silicone rubber plugs and their contents were subjected to vigorous mixing. Desorption with 0.5 ml of benzene was followed by gas chromatographic analysis. Reference solution was prepared by combining 1 μl of the same nitrobenzene solution with 0.5 ml of benzene. Desorption was essentially complete within a few minutes but the sample should be stirred or shaken occasionally. An average value for the desorption coefficient was about 100%.

Dynamic adsorption of nitrobenzene. The setup described previously was equipped additionally with a bubbler absorber to moisten the air. The tubes were filled with two sections of Chromosorb 102, 50 mg each. Glass wool or woven glass cloth was used for the plugs in front, between and after the sorbent sections. A known amount of nitrobenzene dissolved in methanol was introduced into the stream of air flowing at a rate of 80–100 l h^{-1}. About 100 l of air was aspired. As previously, 0.5 ml of benzene was used for desorption.

Based on the results of 6 measurements the desorption coefficient was found to be 97.5±4% independently of the amount of nitrobenzene within the range 0.6–6.0 μg; nor was the storage of the tubes, in darkness and at room temperature for a period of up to 4 days, of any effect.

Desorption of aniline. Aniline adsorbed on Chromosorb G coated with orthophosphoric acid was desorbed with benzene after addition of 0.1 mol l^{-1} water solution of NaOH. Such a concentration of alkali was found to be sufficient. Increase in NaOH concentration up to 2 mol l^{-1} had no effect on the recovery. Like in the case of nitrobenzene the desorption coefficient for aniline, 82±6%, was found to depend

neither on the amount of aniline, within the range 0.5–5.1 μg, nor on the time of prolonged storage (up to 4 days). More replicate analyses should result in considerable improvement of precision of recovery determination.

It is worth noting that toluene can replace benzene as desorbing solvent without any loss in desorption efficiency. If a great number of samples is to be handled, the use of less toxic toluene is recommended. Otherwise, benzene is more convenient; its purification is much easier and there are no problems with tailing.

Gas chromatographic analysis. While gas chromatographic determination of nitrobenzene presents no difficulties, that of aniline does. Even though packed columns can be used [47], adsorption of the polar aniline on the solid support results in asymmetric peaks. Apparently, heavy metallic centres present on the surface of the support form complexes with aniline. Thus, capillary rather than packed columns were used; typically apolar HP-1 and very weakly polar SPB-5 column. Peaks for aniline and nitrobenzene were well resolved, narrow and symmetric. Tailing of the large benzene peak was not a problem.

The operating conditions were as follows: carrier gas, helium at a flow rate of 10 ml min^{-1}; split mode 1/1; injection port, 250°C; detectors, 280°C; flame ionization detector, 50 ml min^{-1} H_2, 500 ml min^{-1} air; column temperature, 50°C for 2 min, increased at 10°C min^{-1} to 200°C, then held for 10 min; sample volume 2 μl; make-up gas for ECD, nitrogen at a flow rate of 150 ml min^{-1}.

The limit of determination for nitrobenzene is 1 μg m^{-3} for FID and 0.1 μg m^{-3} for ECD, assuming a 100 l air sample; desorption with 0.5 ml of benzene; desorption coefficient, 100%; a signal generated that is at least five times the noise. The noise is defined as the $\pm\sigma$ envelope of short-term fluctuations in background current measured for a period of the order of 1 min. The corresponding limit of determination for aniline is 2 μg m^{-3} on the assumption of 80% desorption coefficient.

Field testing

Nitrobenzene. The method was tested under severe conditions. Very polluted atmospheric air sampled in close vicinity of a busy highway contained lots of chemicals that could interfere with nitrobenzene determination. Two tubes, each with two sections of 50 mg of Chromosorb 102, were aspired for 1 h to reach the saturation level for big city pollutants. Next, 0.6 μg of nitrobenzene was adsorbed onto Chromosorb in one of the tubes using the experimental setup described previously. The second tube was let stand as blank. Extraction with 0.5 ml of benzene followed. Gas chromatographic analysis employed both the selected columns and flame ionization as well as electron capture detection. Nitrobenzene introduced was successfully determined within the limits of analytical error: nitrobenzene sampled, 0.60 μg; nitrobenzene determined using HP-1 column and FID, 0.63 μg; nitrobenzene determined using SPB-5 column and FID, 0.59 μg; nitrobenzene determined using SPB-5 column and ECD, 0.67 μg.

Another test involved air polluted by the dye factory which uses nitrobenzene as a raw material. The results are shown in Table 1 and the chromatograms of interest in Figs. 1 and 2. The agreement between the results for both the columns is most satisfactory.

Table 1. Field testing indicating locations of the sampler (concentrations are given in μg m^{-3})

Sample, location	HP-1, FID	SPB-5, ECD
Nitrobenzene		
Dye factory, sewage treatment facilities	193	192
Dye factory, outside the fenced area	1.5	1.8
Aniline		
Cokery, at the outlet of coke battery vents	6.3	6.1

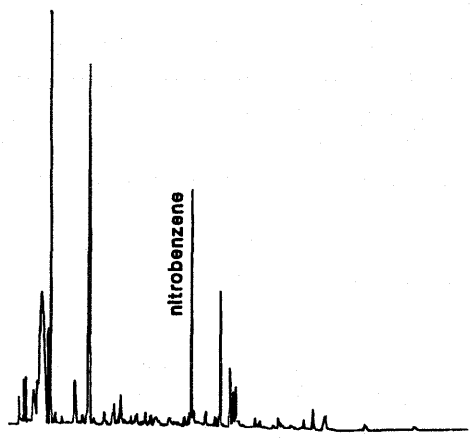

Figure 1. Chromatogram of air sampled outside the fenced area of the dye factory which uses nitrobenzene as a raw material

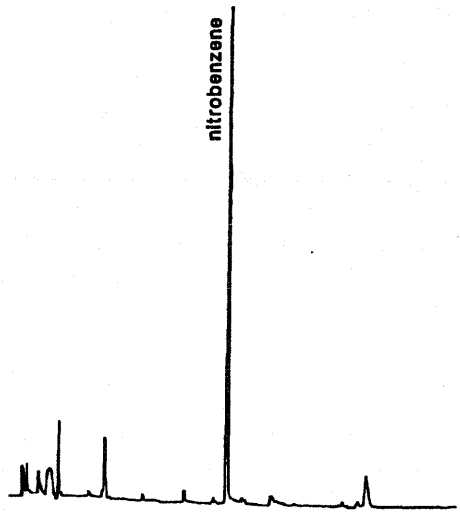

Figure 2. Chromatogram of the calibration solution of nitrobenzene in benzene

Aniline. The procedure for aniline testing was analogous to that used for nitrobenzene. Heavily polluted big city air was aspired through the two tubes filled with Chromosorb G coated with orthophosphoric acid. 0.6 μg of aniline was adsorbed onto one of the tubes while another one served as blank. The analysis for aniline yielded expected results: aniline sampled, 0.6 μg; aniline determined using HP-1 column and FID, 0.63 μg; aniline determined using SPB-5 column and FID, 0.59 μg. The value

of desorption coefficient was accounted for in these estimations. Another test involved air sampled at the cokery. This air is polluted with chemicals that would overlap aniline peak using the columns recommended in this work. However, the results for both the columns agree with each other as can be seen in Table 1. The chromatograms are shown in Figs. 3 and 4. Inspection of figures shows that Chromosorb G doped with orthophosphoric acid is very selective toward aniline; interfering chemicals are not basic and do not undergo any sorption.

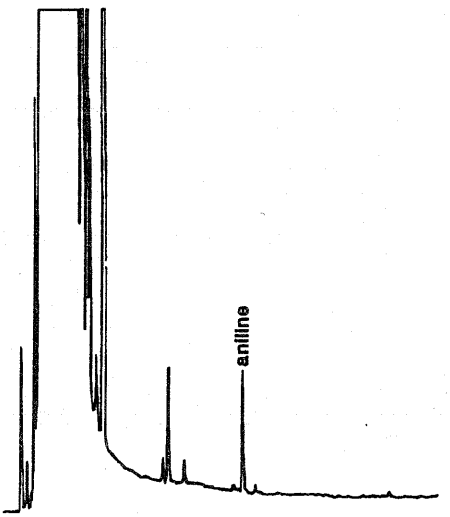

Figure 3. Chromatogram of the air vented by the coke oven battery

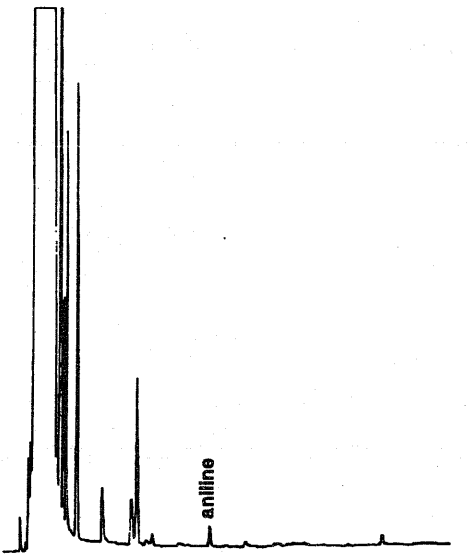

Figure 4. Chromatogram of the air sampled in downtown Warsaw spiked with aniline

Precision and accuracy

Qualitative analysis. Retention times for both aniline and nitrobenzene were found to be stable to within 0.1% with respect to the mean value estimated for the long series of measurements. Experimental scatter of the retention times may necessarily be larger, depending on the equipment used and care taken by analysts, but should not exceed 0.2–0.3%.

Quantitative analysis. Several errors contribute to the total error of analysis.

The accuracy of the method depends appreciably upon collection efficiencies and desorption efficiencies. As a negligible amount of nitrobenzene or aniline has always been detected on the backup section, the collection efficiency of the tube must be essentially 100%. Desorption efficiencies for the range 0.5–6.0 μg are burdened with ±6% and ±4% errors for aniline and nitrobenzene, respectively (estimates based on 6 measurements).

The precision of the chromatographic analysis is quite dependent upon the precision and sensitivity of the technique used to quantitate gas chromatographic peaks of samples and calibration standards. Five consecutive measurements of the calibration solution yielded ±9.6% and 8.3% errors for aniline and nitrobenzene, respectively, using Student parameter $t = 2.776$ at the 95% confidence level.

The error of standard preparations can be ±5% while that of benzene dosage no more than +1%.

The air aspirator used should be able to perform uniformly to within ±3%.

The total error is approximately ±12% of the amount determined from repeated analysis of several standards.

Conclusions

Nitrobenzene and aniline can be determined in the ambient air at the concentration levels below permissible exposure limit. The analytical procedure involves sorption of nitrobenzene and aniline on Chromosorb 102 and Chromosorb G doped with orthophosphoric acid, respectively. Desorption with benzene yields recovery 97.5±4% and 82±6% for nitrobenzene and aniline, respectively. In the latter case desorption is facilitated by alkalization of the medium. Desorption is followed by capillary gas chromatographic analysis. The limit of determination for nitrobenzene is 1 μg m^{-3} using flame ionization detection, and decreases to 0.1 μg m^{-3} using electron capture detection. Aniline features a larger value of 2 μg m^{-3}. Such a sensitivity is more than sufficient for routine monitoring of atmospheric air.

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