

Environmental monitoring of phenolic pollutants in water by cloud point extraction prior to micellar electrokinetic chromatography

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Abstract Many aromatic compounds can be found in the environment as a result of anthropogenic activities and some of them are highly toxic. The need to determine low concentrations of pollutants requires analytical methods with high sensitivity, selectivity, and resolution for application to soil, sediment, water, and other environmental samples. Complex sample preparation involving analyte isolation and enrichment is generally necessary before the final analysis. The present paper outlines a novel, simple, low-cost, and environmentally friendly method for the simultaneous determination of *p*-nitrophenol (PNP), *p*-aminophenol (PAP), and hydroquinone (HQ) by micellar electrokinetic capillary chromatography after preconcentration by cloud point extraction. Enrichment factors of 180 to 200 were achieved. The limits of detection of the analytes for the preconcentration of 50-ml sample volume were $0.10 \mu\text{g L}^{-1}$ for PNP, $0.20 \mu\text{g L}^{-1}$ for PAP, and $0.16 \mu\text{g L}^{-1}$ for HQ. The optimized procedure was applied to the determination of phenolic pollutants in natural waters from San Luis, Argentina.

Keywords Micellar electrokinetic chromatography · Cloud point extraction · *p*-nitrophenol · *p*-aminophenol · Hydroquinone.

Introduction

There has been growing concern for public health and environmental safety over the last few decades. Introduction of toxic pollutants can have a severe impact on many organisms in every ecosystem. *p*-Nitrophenol (PNP) is an important fine chemical intermediate, serving as a precursor of pharmaceuticals and pesticides. Diesel fuel and gasoline exhaust also contain PNP that enters water bodies through rainwater [1]. PNP has been selected as one of the persistent, bioaccumulative, and toxic chemicals by the US Environmental Protection Agency [2]. Due to its harmful effects, wastewaters containing PNP have to be treated before being discharged to receiving water bodies [3–7]. The *p*-aminophenol (PAP) is recognized as a serious environmental pollutant; its target sites in humans are blood and kidney [8, 9]. PAP is used as an intermediate in the production of medicines such as clofibrates and paracetamol. PAP is also used in manufacturing azo, sulfur, acid wool, and leather dyes. It can be used as a photograph developer, a rubber autoxidation agent, and a petroleum additive [9]. As a result, large amounts of PAP may enter the environment as a pollutant.

Hydroquinone (HQ) has a variety of uses principally associated with its action as a reducing agent and its water solubility. It is a major component in most photographic developers. It is also used as a raw material for the synthesis of herbicides, rubber antioxidants, and dye stuffs. HQ, which is produced in large amounts and widely used, must be considered as an environmental

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contaminant. Its acute and chronic toxicity toward higher terrestrial organisms is moderate. Although HQ is estimated to be non-mutagenic by the Ames test, it induces chromosome aberrations or karyotypic effects in eukaryotic cells [10].

Establishing simple, fast, low-cost, sensitive, and selective analytical methods for extraction and determination of pollutants in the environment is one of the main lines of research in environmental chemistry. Recent studies have demonstrated that micellar systems constitute a real alternative to organic solvents for use as extractants of organic pollutants from liquid and solid environmental samples [11].

There are several methods to determine phenols in water and these include gas and liquid chromatography [12, 13]. However, these compounds are present in the environment in low concentrations. Therefore, an enrichment step needs to be carried out prior to separation and detection. Commonly used methods for sample preconcentration are liquid–liquid (LLE) and solid-phase extraction (SPE) [14, 15]. The major disadvantage of LLE is the use of large volumes of high-purity organic solvents, in view of their toxicity and high cost. On the other hand, there is an increasing tendency to replace LLE by SPE and solid-phase microextraction. Several sorbents have been tested for determining pesticides and phenolic compounds. The main problems encountered with SPE are matrix effects when it is used to analyze tap, surface, and river waters. Indeed, the considerable amount of time needed and manual operations involved have to be considered for SPE and LLE. Sample throughput is low and the economic expense is high. Laborious operations such as conditioning, washing, elution, and solvent evaporation are needed [16].

Other methodologies have been developed with the purpose of eliminating or, at least, minimizing the use of organic solvents and simplifying the operating procedure. Surfactant aggregates, together with ionic liquids, are being recognized as having advantages as extractants in certain situations. During the past few years, cloud point extraction (CPE) has shown promise as a preconcentration technique because of its versatility, simplicity, low cost, safety relative to organic solvents, and green chemistry features. Aqueous solutions of some surfactants have been used in CPE of different species prior to their determination using several techniques [17–21]. In principle, the surfactant-rich phase can be used to separate and/or preconcentrate different analytes before their injection into any hydrodynamic analytical system. CPE is thus particularly useful for high-performance liquid chromatography (HPLC), flow injection analysis, and capillary electrophoresis (CE) [22–24].

Micellar electrokinetic chromatography (MEKC) was first described by Terabe et al. [25] in order to enhance the electrophoretic separation of neutral low-molecular-weight

compounds by the introduction of a surfactant such as sodium dodecyl sulfate (SDS) to an aqueous buffer at a concentration above the critical micellar concentration. This enables the formation of a stable micellar phase that functions as a pseudo-stationary phase and partitions the analyte with the aqueous phase. MEKC has become prevalent as a powerful separation technique for organic environmental pollutants [26, 27].

The purpose of the present paper is to demonstrate, for the first time, the feasibility of coupling a cloud point methodology to MEKC for the preconcentration–simultaneous determination of PNP, PAP, and HQ in environmental water samples for the routine analysis of phenolic pollutants, providing a sensitive and robust method with minimal sample handling and high reproducibility.

Materials and methods

Instrumentation

A Beckman P/ACE MDQ instrument (Beckman Instruments, Fullerton, CA, USA) equipped with a diode array detector and a data handling system comprised of an IBM PC and P/ACE System MDQ Software was used. The fused silica capillaries were obtained from MicroSolv Technology Corporation and had the following dimensions: 47-cm total length, 40-cm effective length, 75- μ m inner diameter, and 375- μ m outer diameter. The temperature of the capillary and the samples was maintained at 25 °C. The pH of the electrolyte was measured by an Orion 940 pH meter equipped with a glass-combined electrode. All the glassware used was previously washed with a 10% *v/v* HNO₃/water solution and then with ultrapure water.

Chemicals

The water used in all studies was ultrapure water (18 M Ω cm) obtained from a Barnstead Easy pure RF compact ultrapure water system. The structure and formula of the compounds studied are shown in Fig. 1. *p*-Nitrophenol, *p*-aminophenol, and hydroquinone were purchased from Sigma Chemical Co. (St. Louis, MO, USA) and methanol and acetonitrile (ACN; HPLC grade) were from Merck (Buenos Aires, Argentina). SDS, polyoxyethylene (7.5) nonylphenyl ether (PONPE 7.5), and polyoxyethylene (10) nonylphenyl ether (PONPE 10) were supplied by Tokyo Kasei Industries (Chuo-Ku, Tokyo, Japan). Sodium tetraborate (Na₂B₄O₇·10H₂O) was acquired from Mallinckrodt (St. Louis, MO, USA). All other reagents and solvents were of analytical grade quality.

Solution A As it is not possible to obtain a real aqueous solution of the surfactant PONPE 7.5 (cloud point below

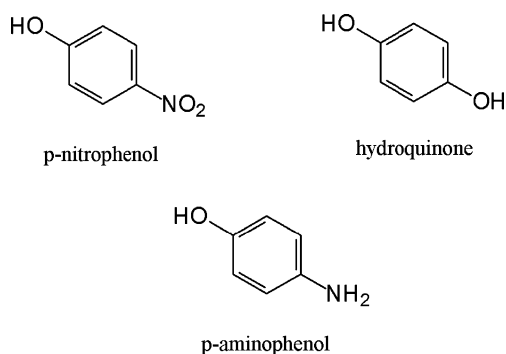


Fig. 1 Chemical structure of the three environmental pollutants

room temperature), it was experimentally convenient to prepare a mother solution as follows: 10 g of PONPE 7.5, 10.0 mL of 1 mol L⁻¹ NaClO₄, and 40 mL of distilled ethanol (Merck, Darmstadt, Germany) were mixed and made up to 100 mL with ultrapure water. Under these conditions, an optimal preconcentration factor was obtained.

Water samples

For this study, rainwater and river water from San Luis Province were analyzed. In September 2007, four rainwater samples were collected by means of a device consisting of a glass funnel with a 5-L glass bottle. After 1 day, the water sample was transported into the laboratory. The volume of each of the rainwater samples collected was 5 L.

The industrial zone of San Luis is located at the south of the Capital of San Luis, in the Cuyo region of Argentina. Twelve water samples were collected from the *Río Seco* of San Luis at a depth of 20 cm. The volume of each of the water sample collected was 1 L.

All samples were collected free of air bubbles in dark glass flasks. The samples were stored in the dark at a temperature of approximately 4 °C and were analyzed within 2 weeks of sampling.

Procedure

Preconcentration steps: cloud point preconcentration procedures

CPE mediated by PONPE 10 A 50-mL aliquot of sample, 20 mL of buffer (20 mM acetate, pH 5.00), 1.00 mL of 0.10 M NaCl (this reagent was added in order to induce a decrease of the system critical point), and 0.20 mL of PONPE 10 were placed in a graduated centrifuge tube. This solution was kept at 70 °C for 10 min for equilibration. After being cooled at 4 °C for 5 min, the surfactant phase,

which had separated, became a viscous gel and the aqueous phase could be poured off.

CPE mediated by PONPE 7.5 Fifty milliliters of sample, 20 mL of buffer (20 mM acetate, pH 5.00), and 1.00 mL solution A were placed in a graduated centrifuge tube. This solution was kept at 30 °C for 10 min for equilibration, centrifuged for 5 min at 3,500 rpm (1,852.26 g), and then cooled at -18 °C for 5 min.

For both cases, a 200-μL aliquot of the surfactant-rich phase was transferred into the CE sample vial and diluted with 300 μL of methanol.

Simultaneous determination of p-nitrophenol, p-aminophenol, and hydroquinone by MEKC

The electrolyte solution was prepared daily and filtered through 0.45-μm Titan Syringe filters (Sri Inc., Eaton Town, NJ, USA). At the beginning of the day, the capillary was conditioned with 0.1 M NaOH for 5 min, followed by water for 5 min, and then with running electrolyte for 10 min before sample injection. To achieve high reproducibility of migration times and to avoid solute adsorption, the capillary was washed between analyses with pure ACN for 5 min, sodium hydroxide for 2 min, followed by water for 2 min, then equilibrated with the running buffer for 4 min. Samples were pressure-injected at the anodic side at 0.5 psi for lengths of time within the range of 3–7 s. The separation was performed at 10 kV. To avoid buffer contamination caused by adsorption of surfactant onto the outer wall of the capillary, the anodic side of the capillary was immersed in ethanol for 2 s immediately after sample injection. A constant voltage was used for all the experiments. Detection was performed at 320 nm. For MEKC, the background electrolyte (BGE) was composed of 20 mM borate buffer (pH 9.0), 20 mM SDS, and acetonitrile (10%). Electroosmotic flow (EOF) determination was performed by using acetone as an EOF marker, prepared by diluting 1 mL of acetone with the BGE and sonicating for 5 min prior to injection. This solution was injected separately for determination of EOF after ten successive sample injections.

Results and discussion

Development of the preconcentration step

The effect of several experimental parameters upon extraction and sensitivity have been thoroughly evaluated and optimized. A summary of the optimal conditions is shown in Table 1.

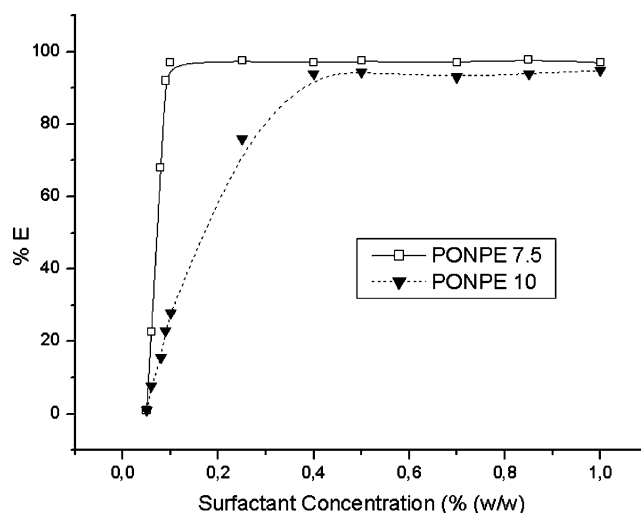
Table 1 Experimental optimized parameters cloud point preconcentration conditions

	PONPE 7.5	PONPE 10
Final volume	53.50 ml	53.50 ml
Extraction pH	5.00	5.00
Surfactant concentration	0.20% w/w	0.50% w/w
Ethanol concentration	0.40% v/v	—
NaCl 0.1 M	—	1 ml
Equilibration temperature	30 °C	70 °C
Equilibration time	10 min	10 min
Centrifugation time	5 min	—
Cooling temperature	−18 °C	4 °C
Diluting agent	Methanol	Methanol
Percentage of dilution	40% v/v	40% v/v

Effect of pH The effect of pH upon sensitivity and extraction parameters was tested within the range of pH 1.50–10.00. The whole combined CPE–MECK procedure was carried out for both surfactants on a synthetic water sample spiked with the target analytes. The analyte signals were monitored by MECK while changing the pH of the sample solution, keeping all other parameters constant. Phenol compounds extraction begins at pH 2.60 and starts to decrease at pH 8.20, showing a plateau for the pH range 3.00–8.00. Considering these results, the selected pH was 5.00 for both surfactants.

Surfactant concentration The effects of PONPE 10 and PONPE 7.5 concentrations upon extraction efficiency were studied within surfactant concentration range 0.05–1.00% w/w. Highly satisfactory extractions were observed for PNP, PAP, and HQ for amphiphile concentrations higher than 0.10% and 0.40% w/w for PONPE 7.5 and PONPE 10, respectively. In order to achieve a good preconcentration factor, a 0.20% (w/w; PONPE 7.5) and 0.50% (w/w; PONPE 10) surfactant concentrations were chosen as optimal. Results for HQ are shown in Fig. 2.

Selection of the dilution agent for the surfactant-rich phase Different solvents for the surfactant-rich phase were tried so as to select the one producing the optimal results regarding sensitivity. The very high viscosity of the surfactant-rich phase (~20 cP) is markedly decreased with a small amount of an appropriate diluting agent. Nevertheless, the selection of eluent is critical for the coupling of CPE with MECK. From other eluents tested, methanol turned out to be the best one for both surfactants. The best separation parameters, reproducibility and sensitivity, were achieved when a 200-μL aliquot of the surfactant-rich

**Fig. 2** Effect of surfactant concentration on HQ extraction/preconcentration. CPE conditions (PONPE 7.5): pH=5.00; equilibration temperature, 30 °C; centrifugation time, 5 min; diluting agent: methanol. CPE conditions (PONPE 10): pH=5.00; equilibration temperature, 70 °C; diluting agent: methanol. %E: percentage of extraction

phase was transferred into the CE sample vial and diluted with 300 μL of methanol.

Development of the separation conditions

In order to propose a specific and accurate way of analyzing CPE-preconcentrated water samples containing PNP, PAP, and HQ, by MEKC, it is essential to find the best experimental conditions in which the analytes can be separated from each other. The following parameters were consecutively optimized: sample conditioning, pH, BGE composition and concentration, sample and capillary temperatures, and other electrophoretic parameters such as separation voltage and injection parameters (Table 2).

Table 2 MEKC conditions

Capillary	75μm ID; 375μm OD; total length 47cm; effective length 40cm
Cartridge temperature	25 °C
Sample temperature	25 °C
BGE	20 mM Na ₂ B ₄ O ₇ ·10 H ₂ O/20 mM SDS/10% ACN pH=9.00
Voltage	10 Kv
Injection hydrodynamics	3 s, 0.50 PSI
Detection wavelength (nm)	320

The effect of the BGE pH was investigated within the range 6.00–11.00 at a fixed buffer concentration, adjusted with 0.10 mM NaOH or 0.10 mM HCl. It was found that when the pH was increased, resolution also increased, while time analysis decreased. The best results were obtained for a pH 9.00 for both surfactants.

Different BGEs have been tested, but the one producing the best results was sodium tetraborate containing ACN and SDS, pH 9.00. Keeping other parameters constant (pH 9.00, 10 kV, 25 °C), the buffer concentration was varied from 5 to 50 mM. Resolution also increased for higher buffer concentrations, but no appreciable improvements were observed for buffer concentrations above 20 mM.

It has been reported that organic modifiers are very important to improve separation in many systems because they can change the partition coefficient and polarity of the sample. ACN was used as an organic modifier in order to enhance the resolution. Various amounts of ACN (5, 10, 15, 20, 25, and 30% v/v) were added into the 20-mM borate buffer, pH 9.00. The compounds were baseline-separated when 10% v/v of ACN was added. So, a 20-mM borate buffer containing 10% ACN and 20 mM SDS, pH 9.00, was chosen as the BGE as it gave a full separation of the analytes.

Separation of the analytes under optimal conditions is shown in Fig. 3. The injection mode giving the best response concerning reproducibility and linear range was the hydrodynamic mode. Injection parameters were optimized by varying the lengths of sample time (3–7 s) and pressure injections (0.30–0.70 psi) until

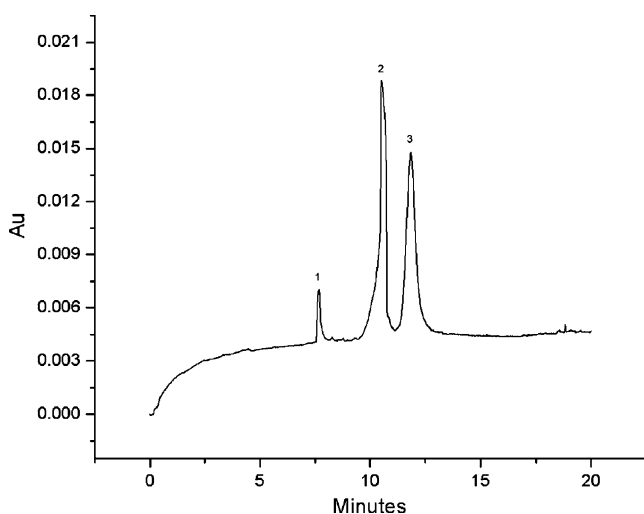


Fig. 3 Electropherogram of a sample with the three pollutants. Conditions: 20 mM borate buffer containing 10% ACN and SDS 20 mM, pH 9.00; capillary, 47 cm full length, 40 cm effective length, 75 μ m ID, 375 μ m OD; hydrodynamic injection at 0.50 PSI, 3 s; 10-kV constant voltage; detection by UV absorbance at 320 nm. (1) hydroquinone; (2) *p*-nitro phenol; (3) *p*-aminophenol

optimum conditions were reached. The best results were obtained with the hydrodynamic injection mode of 0.50 PSI, 3 s.

Due to the high viscosity of the sample, buffer contamination caused by adsorption of surfactant onto the outer wall of the capillary was observed with consequent loss of separation efficiency and reproducibility. Thus, the anodic side of the capillary was immersed in ethanol for 2 s immediately after sample injection.

Separation performance: evaluation of the combined methodology

Figure 3 shows the sample solution electropherogram obtained using the optimized experimental conditions. The migration times of hydroquinone ($pK_a=10.35$), *p*-nitrophenol ($pK_a=7.15$), and *p*-aminophenol ($pK_a=5.3$) were found to be 7.68, 10.52, and 11.85 min, respectively. These migration times did not vary to any considerable degree during and in between analyses (percent relative standard deviation less than 0.80 for the migration time of each peak and less than 2.40 for peak area). The analytes under study were baseline-separated in less than 12 min, giving separation efficiencies of up to 368,029 (PNP) average experimental electrophoretic plates (N).

Extraction percentages higher than 89.50% (Table 3) were achieved when the procedure was carried out under the optimal experimental conditions. Consequently, the enrichment factor (the ratio of the volume of solution used for extraction to the volume of the surfactant-rich phase) achieved for a 50-mL sample volume was: 200-fold (PONPE 7.5) and 180-fold (PONPE 10). The limits of detection of the analytes for the preconcentration of 50 mL sample volume, based on an S/N of 3, were 0.10 μ g L⁻¹ for PNP, 0.20 μ g L⁻¹ for PAP, and 0.16 μ g L⁻¹ for HQ. The calibration graphs using the preconcentration system were linear with a correlation coefficient of 0.9997 (PNP), 0.998 (PAP), and 0.9994 (HQ) at levels near the detection limits up to at least 1.00 mg L⁻¹.

Recovery study

As a certified value for PNP, PAP, and HQ does not exist for any certified reference material of natural water, the method of standard addition was considered as a validation method. Thus, 500 mL of samples (natural water) were collected and divided into ten portions of 50 mL each. The proposed method was applied to six portions and the average quantities of HQ, PNP, and PAP obtained were taken as base values. Then, increasing quantities of the analytes were added to the aliquots of sample and were determined by means of the combined CPE-MEKC method. The results are given in Table 4.

Table 3 CPE efficiency

	%E ^a PONPE 7.5	%E ^a PONPE 10
HQ	96.80	94.20
PNP	99.90	96.30
PAP	89.50	90.50

^a Successive extraction method

: %E percentage of extraction

Sample analysis

The main industrial activities of the area are related to food, metallurgic, plastic, and many chemical industries. In addition, the industrial zone is also affected by extended agricultural activities of the surrounding area and, furthermore, by uncontrolled dumping of household wastes.

Once the conditions for separation and quantification were established, the method was applied to the determination of the three environmental pollutants in river water and the natural water samples mentioned above. The concentrations measured were shown in Table 5. The concentrations measured were in good agreement with those of Niazi and Yazdanipour [28] and Huang et al [29].

Conclusion

MEKC is a hybrid method between electrophoresis and chromatography, which is mainly used for the separation

Table 5 Sample analysis ($n=5$)

	Rainwater ($\mu\text{g/l} \pm \text{SD}$)	River water ($\mu\text{g/l} \pm \text{SD}$)
<i>p</i> -nitrophenol	0.72 ± 0.05	6.90 ± 0.31
<i>p</i> -aminophenol	0.63 ± 0.06	4.08 ± 0.51
Hydroquinone	0.47 ± 0.03	1.06 ± 0.03

of neutral compounds that may normally not be resolved. CPE is a remarkable alternative to conventional solvent extraction which offers an interesting possibility for preconcentrate aromatic pollutants. To our knowledge, this is the first combined CPE–MECK report on the simultaneous direct determination of PNP, PAP, and HQ in synthetic and natural water samples. This procedure has advantages over the traditional liquid–liquid and solid-phase extractions including low cost and safety and also has potential for concentration of a wide variety of analytes of varying nature with high recoveries and high concentration factors. Since it provides a final aqueous solution, it is well suited for CE, especially the MEKC form of CE. Future research is warranted to show the extent of application of this CPE–MEKC method to a wide variety of analyses in environmental samples. Furthermore, considering the chemical nature of the chosen analytes and the preconcentration step (very good efficiency was demonstrated for both surfactants tested) as well as the electrophoretic system, the proposed approach can be applied to the preconcentration–simultaneous determination of other phenolic pollutants.

Table 4 Recovery study of the three compounds in the different extracts

	Added (mg l^{-1})	Found ^a (mg l^{-1})	Found ^a (mg l^{-1})	Precision (mg)
Aliquot I				
HQ	0.00	0.05	–	–
PNP	0.00	0.02	–	–
PAP	0.00	0.05	–	–
Aliquot II				
HQ	0.024	0.073	97.90	$X^c=0.0736$; SD=0.00241; CV=3.27%
PNP	0.015	0.034	98.00	$X^c=0.0347$; SD=0.00158; CV=4.64%
PAP	0.030	0.079	96.70	$X^c=0.0788$; SD=0.00239; CV=3.03%
Aliquot III				
HQ	0.048	0.097	97.92	$X^c=0.0974$; SD=0.00114; CV=1.17%
PNP	0.030	0.049	96.60	$X^c=0.0498$; SD=0.00239; CV=4.8%
PAP	0.060	0.109	99.30	$X^c=0.1086$; SD=0.00114; CV=1.05%
Aliquot IV				
HQ	0.096	0.145	98.96	$X^c=0.1448$; SD=0.00239; CV=1.65%
PNP	0.060	0.079	98.30	$X^c=0.0794$; SD=0.00114; CV=1.44%
PAP	0.120	0.167	97.50	$X^c=0.167$; SD=0.00224; CV=1.34%

^a Mean value ($n=5$)^b [(Found-base)/added] $\times 100$

HQ hydroquinone,
PNP *p*-nitrophenol,
PAP *p*-aminophenol.

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