

## Extraction of hexachloroplatinate from hydrochloric acid solutions with phosphorylated hexane-1,6-diyl polymers

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### ABSTRACT

A series of diols (diethylene glycol, triethylene glycol, butane-1,4-diol and hexane-1,6-diol) were immobilized onto Merrifield resin and subsequently phosphorylated with dialkyl chlorophosphate (alkyl = Me, Et, Bu). The resins bearing hexane-1,6-diyl groups exhibited very good extraction abilities in regard to precious metal chloro complexes like platinum(IV), palladium(II) and rhodium(III). In batch experiments, more than 98% of Pt(IV) is extracted even when the metal and the hydrochloric acid concentration is enhanced significantly. Elution can be achieved with a solution of 0.5 mol L<sup>-1</sup> thiourea in 0.1 mol L<sup>-1</sup> hydrochloric acid. In the presence of other noble metals, platinum(IV) is preferentially bound. The extraction yield decreases in slightly acidic solution in the following order: Pt(IV) ≈ Pd(II) > Rh(III) and changes with increasing hydrochloric acid concentration to Pt(IV) > Pd(II) ≫ Rh(III). At different ratios of metal and acid, the temperature has nearly no influence on the platinum extraction. On slightly acidic media, the extraction of rhodium decreases by 30% when the temperature is increased from 10 °C to 40 °C. When the acid and metal concentration is enhanced, the palladium extraction decreases by 7–9%, depending on the resin.

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### 1. Introduction

The guiding principle to preserve the natural environment and its resources has become an important motivation in our society. At the same time, there is a growing demand for precious metals [1], especially platinum, palladium and rhodium, due to their widespread use in different technological fields such as industrial catalysis, electronic devices, medical purposes, jewellery and automotive catalytic converters [2]. Since the platinum group metals (PGMs) are of a low natural abundance, recovery from secondary materials like spent catalytic converters is a matter of increasing interest [3,4].

The constant search for new PGM extraction processes is also reflected in the numerous review articles published on this topic [5–9], in particular the two main separation methods: solid-phase extraction (SPE) and solvent extraction (SX).

The advantages of SX (compared to SPE) like higher capacity and selectivity are accompanied by a higher consumption of organic solvents (and inevitably waste disposal), a possible loss of extractant and solvent, problems in phase separation or formation of emulsions and third phases [10,11,12a]. These disadvantages can be overcome with SPE materials consisting of a solid support, modified with a selective extracting agent. In most cases, the

ligand is covalently bonded to the resin, which makes a loss of extractant impossible. Due to the insoluble nature of the polymer in the aqueous phase, phase separation becomes easy and the formation of additional phases or emulsions is avoided [6,10,11,13]. Moreover, the kinetics can be enhanced through modification in the resins' matrix like cross-linking, porosity and particle size [6].

In SX of noble metals manifold extracting agents were used: containing oxygen [14], sulphur [15], nitrogen [16–19], nitrogen-sulphur combinations [20–22], or phosphorous. Among these extractants, phosphorous containing ligands like phosphine sulphide [23,24], phosphine oxide [23,25], triphenyl phosphine [26], bisphosphonate [27] and amino phosphonate [28] are widely used.

In a variety of scientific studies dealing with SPE, resins were modified with amine extractants which are often commercially available [29–32]. Ligands containing phosphorous are the second most common extractants used for this kind of solid supports. The solid-phase extraction resins include phosphine sulphides [33,34], tris(2,6-dimethoxyphenyl) phosphine that forms a quarternary phosphonium chloride when immobilized on a solid support [35] and phosphates with additional hydroxyl groups on the spacer (so-called bifunctional polymers) [36]. In addition, there are also resins with the extracting agent impregnated on the solid support, for example di-(2-ethylhexyl) thiophosphoric acid [37], bis(2,4,4-trimethylpentyl) dithiophosphinic acid and bis(3-ethylhexyl) monothio-phosphoric acid [38a]. Currently, a new extraction approach comprises the application of ionic liquids based on trihexyl(tetra-decyl) phosphonium cations with varying anions [39,40].

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Our main research interest is the recovery of PGMs from spent automotive catalytic converters, in particular the recycling of platinum, palladium and rhodium from chloride containing leach liquors. Our aim was to design a new extraction system with high capacities for PGM and a preferred selectivity for platinum, especially in strong hydrochloric acid media. We opted for tributyl phosphate (TBP) which is a well-known solvent extracting agent for platinum, investigated in fundamental research [41–43] and applied in industry [12b,44–46]. This ligand possesses good extraction ability for PGMs and is stable in hydrochloric acid [12b,41,43]. In order to combine the advantages of TBP with the advantages of the SPE method, we immobilized different diols onto Merrifield resin followed by phosphorylation of the modified resins. The length of the spacer and the alkyl groups as well as the kind of spacer have been varied to enhance the loading capacities for the precious metals and to determine the influence on the complex stability in aqueous acidic solutions. Depending on the hydrochloric acid concentration, different aqua chloro complexes are formed. This was used to improve the selectivity and to find optimal conditions for the separation of the PGMs. In model solutions containing one to three of these noble metals, the extraction behaviour of the PGMs was determined systematically. While TBP is known as a solvating extractant [7], in SPE other and additional effects occur, for example ligand substitution reactions and ion exchange. The different extraction tendency of platinum compared to palladium and rhodium in slightly and relatively strong acidic media could be explained by two possible extraction mechanisms. Platinum(IV) tends to form ion pairs due to the lower charge density, whereas palladium undergoes ligand substitution reactions because palladium(II) complexes are more labile [9,47]. The availability of competing groups like chloride ions is also of great importance for the extraction equilibrium of the noble metals platinum(IV), palladium(II) and rhodium(III). The separation of these three precious metals is achieved by considering the influence of different parameters, like the temperature, the concentration of the metals as well as the hydrochloric acid concentration for the selectivity of the individual metals which is determined and presented systematically in this paper.

## 2. Experimental

### 2.1. Reagents and solutions for resin preparation

Merrifield's peptide resin (1% cross-linked with DVB, 100–200 mesh, 1.5–2 mmol Cl per g polymer), hexane-1,6-diol (97%), 1,3-dichloro-5,5-dimethylhydantoin and dibutyl phosphite (96%) were purchased from Sigma–Aldrich. Diethyl phosphite ( $\geq 95\%$ ) and dimethyl phosphite ( $\geq 98\%$ ) were obtained from Fluka. Sodium hydroxide ( $> 97\%$ ), methanol ( $\geq 98.5\%$ ) and acetone ( $\geq 99\%$ ) were received from ProLabo VWR. Ethanol was purchased from Berkel AHK. Tetrabutyl ammoniumbromide ( $>99\%$ ), butane-1,4-diol ( $>99\%$ ), diethylene glycol ( $\geq 99\%$ ), triethylene glycol ( $\geq 99\%$ ), carbon tetrachloride ( $\geq 99.8\%$ ), benzene ( $\geq 99\%$ ), pyridine ( $\geq 99.5\%$ ) were obtained from Merck KGaA. The solvents were used without further purification.

### 2.2. Synthesis

The preparation of the ligands was done according to the literature [48]. 0.2 mol L<sup>-1</sup> of the appropriate dialkyl phosphite was added dropwise to a suspension of 0.1 mol L<sup>-1</sup> 1,3-dichloro-5,5-dimethylhydantoin in 100 mL carbon tetrachloride. The mixture was stirred for 16 h and the emerging solid was filtrated. Then, the solvent was removed and the dialkyl chlorophosphate was distilled in vacuum.

Dimethyl chlorophosphate was obtained as a colourless liquid (yield 51%, 14.74 g). Bp.: 75–77 °C/20 mbar. <sup>1</sup>H NMR (CDCl<sub>3</sub>-d<sub>1</sub>; 300 MHz;  $\delta$  in ppm) 3.77 (s, 6H, —CH<sub>3</sub> proton). <sup>13</sup>C NMR (CDCl<sub>3</sub>-d<sub>1</sub>; 75 MHz;  $\delta$  in ppm) 55.3 (—CH<sub>3</sub> carbon). <sup>31</sup>P NMR (CDCl<sub>3</sub>-d<sub>1</sub>; reference H<sub>3</sub>PO<sub>4</sub>; 121 MHz;  $\delta$  in ppm) 7.83. MS (CHCl<sub>3</sub>) 142, 127, 109, 96, 81, 66.

Diethyl chlorophosphate was received as a colourless liquid (yield 83%, 28.64 g). Bp.: 95 °C/25 mbar. <sup>1</sup>H NMR (CDCl<sub>3</sub>-d<sub>1</sub>; 300 MHz;  $\delta$  in ppm) 4.11 (m, 4H, —CH<sub>2</sub>— protons), 1.25 (t, 6H, —CH<sub>3</sub> protons). <sup>13</sup>C NMR (CDCl<sub>3</sub>-d<sub>1</sub>; 75 MHz;  $\delta$  in ppm) 65.5 (—CH<sub>2</sub>— carbon), 15.3 (—CH<sub>3</sub> carbon). <sup>31</sup>P NMR (CDCl<sub>3</sub>-d<sub>1</sub>; reference H<sub>3</sub>PO<sub>4</sub>; 121 MHz;  $\delta$  in ppm) 4.69. MS (CHCl<sub>3</sub>) 155, 142, 127, 111, 99, 91, 81.

Dibutyl chlorophosphate was obtained as a colourless liquid (yield 81%, 37.04 g). Bp.: 52–53 °C/1.3–1.1 × 10<sup>-2</sup> mbar. <sup>1</sup>H NMR (CDCl<sub>3</sub>-d<sub>1</sub>; 300 MHz;  $\delta$  in ppm) 4.04 (m, 4H, —CH<sub>2</sub>— protons next to phosphor atom), 1.56 (quin, 4H, —CH<sub>2</sub>— protons between other methylene groups), 1.28 (se, 4H, —CH<sub>2</sub>— protons next to methyl group), 0.79 (t, 6H, —CH<sub>3</sub> protons). <sup>13</sup>C NMR (CDCl<sub>3</sub>-d<sub>1</sub>; 75 MHz;  $\delta$  in ppm) 69.0 (—CH<sub>2</sub>— carbon next to phosphor atom), 31.4 (—CH<sub>2</sub>— carbon between other methylene groups), 18.2 (—CH<sub>2</sub>— carbon next to methyl group), 13.0 (—CH<sub>3</sub> carbon). <sup>31</sup>P NMR (CDCl<sub>3</sub>-d<sub>1</sub>; reference H<sub>3</sub>PO<sub>4</sub>; 121 MHz;  $\delta$  in ppm) 5.14. MS (CHCl<sub>3</sub>) 229, 173, 117, 83, 56, 41.

The diols were immobilized onto the Merrifield's peptide resin following literature procedures [49]. The resin was washed with benzene, acetone and ethanol, then further purified in a soxhlet extractor with ethanol. Afterwards, 6 g of the resin were stirred with 100 mL of benzene for 16 h due to swelling. 0.06 mol L<sup>-1</sup> of the base sodium hydroxide and 0.004 mol L<sup>-1</sup> of the phase transfer catalyst tetrabutylammonium bromide were added to the solution 0.06 mol L<sup>-1</sup> of the appropriate spacer (hexane-1,6-diol, butane-1,4-diol, diethylene glycol or triethylene glycol). The suspension was left to stir at 60 °C for 6 h and then at room temperature for 16 h under a nitrogen atmosphere. The resin was washed with methanol, water, acetone, ethanol and was further purified in a soxhlet extractor with ethanol. Afterwards, the modified resin was allowed to dry at room temperature. All resins exhibited a beige colour.

4-Hydroxybutoxy modified Merrifield resin (**1**): yield of 91% (7.23 g). EA (%): C 86.16, H 7.71, O 4.31. FT-IR (KBr, cm<sup>-1</sup>): 3436 (ν O—H), 3024 (ν aromatic), 2912 (ν<sub>as</sub> CH<sub>2</sub>), 2848 (ν<sub>s</sub> CH<sub>2</sub>), 1601 (ν aromatic C—C), 1492 (ν aromatic C—C), 1451 (δ CH<sub>2</sub>), 1091 (ν C—O), 1061 (ν<sub>as</sub> C—O), 1027 (ν<sub>s</sub> C—O), 840 (δ<sub>oop</sub> aromatic-H), 818, 755 (ν CH<sub>2</sub>), 696 (δ aromatic-H).

6-Hydroxyhexoxy modified Merrifield resin (**2**): yield of 80% (5.58 g). EA (%): C 85.59, H 7.29, O 1.16. FT-IR (KBr, cm<sup>-1</sup>): 3441 (ν O—H), 3024 (ν aromatic), 2919 (ν<sub>as</sub> CH<sub>2</sub>), 2849 (ν<sub>s</sub> CH<sub>2</sub>), 1601 (ν aromatic C—C), 1492 (ν aromatic C—C), 1450 (δ CH<sub>2</sub>), 1264 (δ<sub>ip</sub> C—O), 1027 (ν C—O), 836 (δ<sub>oop</sub> aromatic-H), 823, 757 (ν CH<sub>2</sub>), 697 (δ aromatic-H).

1-Hydroxy-3,5-dioxapentyl modified Merrifield resin (**3**): yield of 88% (6.02 g). EA (%): C 84.47, H 7.59, O 5.9. FT-IR (KBr, cm<sup>-1</sup>): 3433 (ν O—H), 3024 (ν aromatic), 2971 (ν<sub>as</sub> CH<sub>2</sub>), 2845 (ν<sub>s</sub> CH<sub>2</sub>), 1601 (ν aromatic C—C), 1493 (ν aromatic C—C), 1451 (δ CH<sub>2</sub>), 1088 (ν C—O), 1048 (ν C—O), 842 (δ<sub>oop</sub> aromatic-H), 818, 755 (ν CH<sub>2</sub>), 696 (δ aromatic-H).

1-Hydroxy-3,6,8-trioxaocetyl modified Merrifield resin (**4**): yield of 87% (6.41 g). EA (%): C 82.71, H 7.88, O 8.47. FT-IR (KBr, cm<sup>-1</sup>): 3457 (ν O—H), 3025 (ν aromatic), 2907 (ν<sub>as</sub> CH<sub>2</sub>), 2848 (ν<sub>s</sub> CH<sub>2</sub>), 1601 (ν aromatic C—C), 1493 (ν aromatic C—C), 1451 (δ CH<sub>2</sub>), 1349 (δ<sub>ip</sub> C—OH), 1093 (ν C—O), 1029 (ν C—O), 817 (δ<sub>oop</sub> aromatic-H), 749 (ν CH<sub>2</sub>), 698 (δ aromatic-H).

The ligand was connected to the spacer modified resin according to the literature [50]. Six gram of the dried spacer modified resin was mixed with pyridine and 0.12 mol L<sup>-1</sup> of the appropriate dialkyl chlorophosphate was added dropwise. After stirring over

night, the resin was filtered and washed with methanol, methanol/water mixture (1/1) and water. The resin was dried in an exsiccator. All resins exhibited a beige colour.

Dimethyl-(butane-1,4-diyl) phosphate polymer (**1a**): yield of 91% (7.23 g). EA (%): C 74.69, H 7.18, O 9.70. UV-Vis (mmol g<sup>-1</sup>): P 1.39. FT-IR (KBr, cm<sup>-1</sup>): 3024 (ν aromatic), 2921 (ν<sub>as</sub> CH<sub>2</sub>), 2851 (ν<sub>s</sub> CH<sub>2</sub>), 1601 (ν aromatic C—C), 1493 (ν aromatic C—C), 1452 (δ CH<sub>2</sub>), 1273 (ν P=O), 1046 (ν P—O—C), 846 (ν P—O—C), 756 (ν CH<sub>2</sub>), 697 (δ aromatic-H).

Diethyl-(butane-1,4-diyl) phosphate polymer (**1b**): yield of 88% (7.28 g). EA (%): C 75.87, H 7.98, O 8.28. UV-Vis (mmol g<sup>-1</sup>): P 1.26. FT-IR (KBr, cm<sup>-1</sup>): 3025 (ν aromatic), 2920 (ν<sub>as</sub> CH<sub>2</sub>), 2850 (ν<sub>s</sub> CH<sub>2</sub>), 1601 (ν aromatic C—C), 1493 (ν aromatic C—C), 1452 (δ CH<sub>2</sub>), 1275 (ν P=O), 1028 (ν P—O—C), 817 (ν P—O—C), 755 (ν CH<sub>2</sub>), 697 (δ aromatic-H).

Dibutyl-(butane-1,4-diyl) phosphate polymer (**1c**): yield of 84% (7.52 g). EA (%): C 76.52, H 7.79, O 7.16. UV-Vis (mmol g<sup>-1</sup>): P 1.15. FT-IR (KBr, cm<sup>-1</sup>): 3025 (ν aromatic), 2922 (ν<sub>as</sub> CH<sub>2</sub>), 2850 (ν<sub>s</sub> CH<sub>2</sub>), 1601 (ν aromatic C—C), 1493 (ν aromatic C—C), 1452 (δ CH<sub>2</sub>), 1278 (ν P=O), 1026 (ν P—O—C), 817 (ν P—O—C), 757 (ν CH<sub>2</sub>), 697 (δ aromatic-H).

Dimethyl-(hexane-1,6-diyl) phosphate polymer (**2a**): yield of 99% (8.20 g). EA (%): C 71.16, H 6.69, O 12.10. UV-Vis (mmol g<sup>-1</sup>): P 1.88. FT-IR (KBr, cm<sup>-1</sup>): 3024 (ν aromatic), 2919 (ν<sub>as</sub> CH<sub>2</sub>), 2846 (ν<sub>s</sub> CH<sub>2</sub>), 1631 (ν aromatic C—C), 1601 (ν aromatic C—C), 1490 (ν aromatic C—C), 1451 (δ CH<sub>2</sub>), 1218 (ν P=O), 1026 (ν P—O—C), 856 (ν P—O—C), 748 (ν CH<sub>2</sub>), 697 (δ aromatic-H).

Diethyl-(hexane-1,6-diyl) phosphate polymer (**2b**): yield of 92% (7.92 g). EA (%): C 75.18, H 7.03, O 8.26. UV-Vis (mmol g<sup>-1</sup>): P 0.93. FT-IR (KBr, cm<sup>-1</sup>): 3024 (ν aromatic), 2918 (ν<sub>as</sub> CH<sub>2</sub>), 2848 (ν<sub>s</sub> CH<sub>2</sub>), 1631 (ν aromatic C—C), 1600 (ν aromatic C—C), 1490 (ν aromatic C—C), 1450 (δ CH<sub>2</sub>), 1212 (ν P=O), 1027 (ν P—O—C), 860 (ν P—O—C), 757 (ν CH<sub>2</sub>), 697 (δ aromatic-H).

Dibutyl-(hexane-1,6-diyl) phosphate polymer (**2c**): yield of 59% (5.48 g). EA (%): C 76.86, H 7.22, O 6.56. UV-Vis (mmol g<sup>-1</sup>): P 0.54. FT-IR (KBr, cm<sup>-1</sup>): 3023 (ν aromatic), 2917 (ν<sub>as</sub> CH<sub>2</sub>), 2849 (ν<sub>s</sub> CH<sub>2</sub>), 1630 (ν aromatic C—C), 1600 (ν aromatic C—C), 1489 (ν aromatic C—C), 1450 (δ CH<sub>2</sub>), 1212 (ν P=O), 1026 (ν P—O—C), 859 (ν P—O—C), 756 (ν CH<sub>2</sub>), 697 (δ aromatic-H).

Dimethyl-(3-oxapentane-1,5-diyl) phosphate polymer (**3a**): yield of 76% (6.18 g). EA (%): C 72.68, H 6.87, O 10.29. UV-Vis (mmol g<sup>-1</sup>): P 1.44. FT-IR (KBr, cm<sup>-1</sup>): 3024 (ν aromatic), 2918 (ν<sub>as</sub> CH<sub>2</sub>), 2852 (ν<sub>s</sub> CH<sub>2</sub>), 1632 (ν aromatic C—C), 1601 (ν aromatic C—C), 1492 (ν aromatic C—C), 1451 (δ CH<sub>2</sub>), 1273 (ν P=O), 1022 (ν P—O—C), 848 (ν P—O—C), 755 (ν CH<sub>2</sub>), 696 (δ aromatic-H).

Diethyl-(3-oxapentane-1,5-diyl) phosphate polymer (**3b**): yield of 67% (5.67 g). EA (%): C 76.82, H 7.57, O 10.03. UV-Vis (mmol g<sup>-1</sup>): P 1.18. FT-IR (KBr, cm<sup>-1</sup>): 3025 (ν aromatic), 2918 (ν<sub>as</sub> CH<sub>2</sub>), 2851 (ν<sub>s</sub> CH<sub>2</sub>), 1601 (ν aromatic C—C), 1493 (ν aromatic C—C), 1453 (δ CH<sub>2</sub>), 1274 (ν P=O), 1101 (ν CH<sub>3</sub>), 1027 (ν P—O—C), 969, 817 (ν P—O—C), 755 (ν CH<sub>2</sub>), 697 (δ aromatic-H).

Dibutyl-(3-oxapentane-1,5-diyl) phosphate polymer (**3c**): yield of 67% (6.13 g). EA (%): C 77.96, H 7.85, O 8.69. UV-Vis (mmol g<sup>-1</sup>): P 0.95. FT-IR (KBr, cm<sup>-1</sup>): 3025 (ν aromatic), 2919 (ν<sub>as</sub> CH<sub>2</sub>), 2851 (ν<sub>s</sub> CH<sub>2</sub>), 1601 (ν aromatic C—C), 1493 (ν aromatic C—C), 1452 (δ CH<sub>2</sub>), 1278 (ν P=O), 1025 (ν P—O—C), 816 (ν P—O—C), 756 (ν CH<sub>2</sub>), 697 (δ aromatic-H).

Dimethyl-(3,6-dioxaoctane-1,8-diyl) phosphate polymer (**4a**): yield of 81% (7.02 g). EA (%): C 72.79, H 7.18, O 0.73. UV-Vis (mmol g<sup>-1</sup>): P 1.38. FT-IR (KBr, cm<sup>-1</sup>): 3024 (ν aromatic), 2907 (ν<sub>as</sub> CH<sub>2</sub>), 2849 (ν<sub>s</sub> CH<sub>2</sub>), 1648 (ν aromatic C—C), 1601 (ν aromatic C—C), 1493 (ν aromatic C—C), 1452 (δ CH<sub>2</sub>), 1283 (ν P=O), 1095 (ν CH<sub>3</sub>), 1029 (ν P—O—C), 973, 846 (ν P—O—C), 818, 749 (ν CH<sub>2</sub>), 697 (δ aromatic-H).

Diethyl-(3,6-dioxaoctane-1,8-diyl) phosphate polymer (**4b**): yield of 88% (7.92 g). EA (%): C 76.25, H 7.72, O 11.29. UV-Vis

(mmol g<sup>-1</sup>): P 1.10. FT-IR (KBr, cm<sup>-1</sup>): 3026 (ν aromatic), 2907 (ν<sub>as</sub> CH<sub>2</sub>), 2849 (ν<sub>s</sub> CH<sub>2</sub>), 1601 (ν aromatic C—C), 1493 (ν aromatic C—C), 1453 (δ CH<sub>2</sub>), 1262 (ν P=O), 1100 (ν CH<sub>3</sub>), 1028 (ν P—O—C), 818 (ν P—O—C), 757 (ν CH<sub>2</sub>), 698 (δ aromatic-H).

Dibutyl-(3,6-dioxaoctane-1,8-diyl) phosphate polymer (**4c**): yield of 68% (6.58 g). EA (%): C 77.05, H 7.93, O 10.28. UV-Vis (mmol g<sup>-1</sup>): P 1.02. FT-IR (KBr, cm<sup>-1</sup>): 3026 (ν aromatic), 2921 (ν<sub>as</sub> CH<sub>2</sub>), 2855 (ν<sub>s</sub> CH<sub>2</sub>), 1601 (ν aromatic C—C), 1493 (ν aromatic C—C), 1452 (δ CH<sub>2</sub>), 1279 (ν P=O), 1100 (ν CH<sub>3</sub>), 1028 (ν P—O—C), 817 (ν P—O—C), 758 (ν CH<sub>2</sub>), 698 (δ aromatic-H).

### 2.3. Instrumentation and characterisation of the resins

<sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR analysis was performed on a Bruker Avance 300 NMR spectrometer using CDCl<sub>3</sub>-d<sub>1</sub> as a solvent that was also used as an internal reference for <sup>1</sup>H and <sup>13</sup>C NMR measurements. For <sup>31</sup>P NMR analysis, H<sub>3</sub>PO<sub>4</sub> (85%) was used as an external reference. Elemental analysis (C, H, O) were determined with an Elementar Vario EL elemental analyser. Phosphorous content was determined by the ammonium molybdate method with a Perkin Elmer Lambda 2 UV-Vis spectrometer (wave length of 882.5 nm; cell with path length of 1 cm). EI MS spectra were recorded using a Thermo Scientific DSQII spectrometer in the solvent CHCl<sub>3</sub>. FT-IR-Nexus (Thermo Nicolet) was used to confirm the chemical composition of the different resins by FT-IR spectroscopy (KBr pellets, transmission mode with 32 scans and a resolution of 4 cm<sup>-1</sup>).

### 2.4. Reagents and solutions for batch experiments

Platinum standard solution (1 g L<sup>-1</sup> H<sub>2</sub>[PtCl<sub>6</sub>] in 2 mol L<sup>-1</sup> HCl, equates to 5.13 × 10<sup>-3</sup> mol L<sup>-1</sup> H<sub>2</sub>[PtCl<sub>6</sub>] in 2 mol L<sup>-1</sup> HCl) and rhodium standard solution (1 g L<sup>-1</sup> RhCl<sub>3</sub> in 1 mol L<sup>-1</sup> HCl, equates to 9.72 × 10<sup>-3</sup> mol L<sup>-1</sup> RhCl<sub>3</sub> in 1 mol L<sup>-1</sup> HCl) were obtained from Bernd Kraft GmbH. Palladium standard solution (997 ppm in 5 wt.% HCl, equates to 9.37 × 10<sup>-3</sup> mol L<sup>-1</sup> in 5 wt.% HCl) was purchased from Fluka. Hydrochlorid acid (30%, suprapur) was received from Merck KGaA.

### 2.5. Instrumentation for batch experiments

The solid and the aqueous phases were mixed in an overhead rotation shaker (Reax 2 from Heidolph) and separated by centrifugation (Centrifuge 5416 from Eppendorf). The initial and final metal content of the aqueous phase was determined using an ICP OES (Optima 7300 DV from Perkin Elmer with cyclonic spray chamber and Mira Mist nebulizer) and an S10 autosampler (Perkin Elmer). Extraction experiments with temperature variation were done in an MKR 13 cooling-thermo mixer (HLC).

All pH measurements were done with a WTW 340 pH hand-held metre equipped with a SenTix 21 pH combined electrode (Ag/AgCl with gel filling). Calibration of the system prior to use was performed with standard buffer solutions at pH 4 and 7 (Radiometer Copenhagen).

### 2.6. General procedure for batch experiments

The batch extraction experiments were performed using 50 mg ± 0.5 mg of the dry resin mixed with 5 mL of the appropriate aqueous acidic metal solution. The metal solution was obtained by diluting of the platinum(IV), palladium(II) and rhodium(III) standards in deionised water (Purelab ultra from Elga) or hydrochloric acid in the relevant concentration. The mixed phases were shaken with an overhead rotation shaker for 180 min, if not otherwise stated. In order to examine the temperature dependency a cooling-thermo mixer (1000 rpm) was used for 180 min. For the determination of the equilibrium, samples were mixed for 0, 1,

15, 30, 60, 90, 120, 180 min and for the capacity determination the shaker was employed until equilibrium was reached (60 min for the resin **1c** and 15 min for the resins **2a–2c**). The phases were separated with the help of a centrifuge for 15 min and 4000 rpm.

For elution experiments, the loaded resin was shaken for 180 min with 5 mL of an aqueous acidic thiourea solution. The phase separation procedure was done according to the extraction experiments.

### 2.7. Theoretical parameters

The extraction yield  $E$  was calculated as shown in the following equation:

$$E[\%] = \left( \frac{c_o - c_e}{c_e} \right) \cdot 100 \quad (1)$$

In this equation,  $c_o$  [mg L<sup>-1</sup>] is the concentration of the aqueous acidic metal phase prior to the extraction experiment and  $c_e$  [mg L<sup>-1</sup>] is the concentration afterwards. The subscribed 'o' refers to original and the subscribed 'e' refers to the equilibrium state (or to the concentration after a certain time  $t$ ).

The capacity  $q_e$  was determined using the following equation:

$$Q_e[\text{mg g}^{-1}] = (c_o - c_e) \cdot \left( \frac{V}{m} \right) \quad (2)$$

The volume  $V$  [L] of the aqueous acidic metal solution and the weight  $m$  [g] of the dried resin were needed for Eq. (2). For converting the unit of the capacity to mmol g<sup>-1</sup>, the whole equation has to be divided by the molar mass  $M$  [g mol<sup>-1</sup>].

The distribution coefficient  $D$  is calculated according to the following equation:

$$D [\text{mL g}^{-1}] = \left( \frac{c_o - c_e}{c_e} \right) \cdot \left( \frac{V}{m} \right) \quad (3)$$

The separation factor  $S_2^1$  of metal 1 compared to metal 2 is the ratio of distribution coefficients for both metals, as seen in the following equation:

$$S_2^1 = \frac{D_1}{D_2} \quad (4)$$

The Langmuir isotherm is represented by the following Eq. (5) and in a linearised form by the following equation:

$$q_e = \frac{q_m \cdot K_L \cdot c_e}{1 + k_L \cdot c_e} \quad (5)$$

$$\frac{c_e}{q_e} = \frac{1}{q_m \cdot K_L} + \frac{1}{q_m} \cdot c_e \quad (6)$$

The Langmuir constant  $K_L$  [L mmol<sup>-1</sup>] is the affinity of the binding for a certain metal ion. The maximum adsorption capacity is described as  $q_m$  [mmol g<sup>-1</sup>].

The Freundlich isotherm is represented by the following Eq. (7) and in a linearised form by Eq. (8):

$$q_e = K_F \cdot c_e^{\frac{1}{n}} \quad (7)$$

$$\ln q_e = \ln K_F + \left( \frac{1}{n} \right) \cdot \ln c_e \quad (8)$$

$K_F$  and  $n$  are Freundlich constants referring to the adsorption capacity and the adsorption intensity respectively.

The Langmuir constant  $K_L$  is related to the Gibbs free energy  $\Delta G^0$  and can be expressed according to Eq. (9). The correlation between the enthalpy  $\Delta H^0$ , the entropy  $\Delta S^0$  and the equilibrium constant  $K_L$  is given by the following Van't Hoff Eq. (10):

$$\Delta G^0 = -RT \cdot \ln K_L \quad (9)$$

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (10)$$

In this equation  $R$  is the universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) and  $T$  [K] the temperature.

## 3. Results and discussion

### 3.1. Synthesis and characterisation

#### 3.1.1. Synthesis

A series of phosphorylated polymers was prepared by modification of Merrifield's resins. This commercial resin is based on a copolymer of polystyrene and divinylbenzene which was chloromethylated. The extracting materials were prepared in two steps.

The first synthetic step was the binding of the spacer on the polymer backbone. In order to examine the influence of the spacers length and the composition, four different spacers based on alkanediol (butane-1,4-diol and hexane-1,6-diol) or ethylene glycol (diethylene glycol and triethylene glycol) were used. The reaction was done in the presence of the base sodium hydroxide and the phase transfer catalyst tetrabutylammonium bromide. The diol modified resins were amenable to a further functionalization with phosphate ligands. Subsequently the second step was the phosphorylation of the spacer modified resin with the appropriate dialkyl chlorophosphate (Scheme 1). The nucleophilic substitution was done in pyridine which acts as solvent and removes the acid generated during the reaction.

#### 3.1.2. Characterisation

The modified resins were characterised by elemental analysis (EA) and FT-IR spectroscopy (especially the fingerprint region).

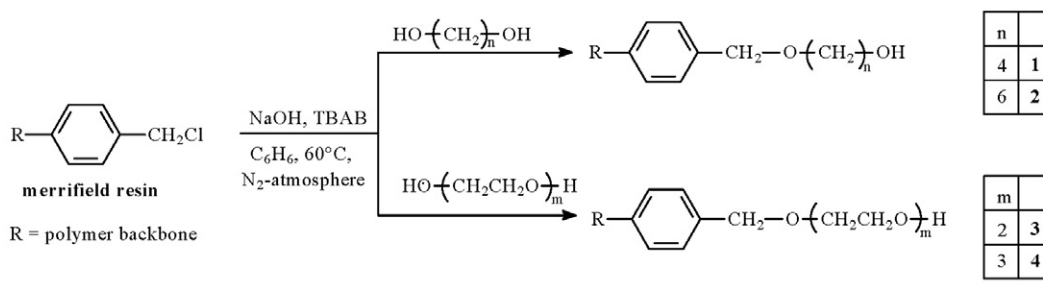
EA affirmed the conversion of the Merrifield's chloromethyl group to the hydroxy alkoxy or hydroxy oxaalkyl groups, respectively. Although, the conversion of the groups is not complete. FT-IR spectra of the Merrifield resin and the spacer modified resins resemble each other due to the same polymer backbone (Fig. 1). The characteristic C–Cl stretching vibration of the Merrifield resin appears in the region of 820 cm<sup>-1</sup> and 600 cm<sup>-1</sup> [51].

Characteristic vibrations of the spacer were found at three different wave numbers. The band between 3650 cm<sup>-1</sup> and 3200 cm<sup>-1</sup> can be attributed to the O–H stretching vibration [49,51] whereas the broadened band between 1260 cm<sup>-1</sup> and 970 cm<sup>-1</sup> can be ascribed to the C–O stretching vibration [49,51] and appears mostly as a duplet (as can be seen in Table 1). In comparison to the FT-IR spectra of the Merrifield resin, these bands seem to be broadened.

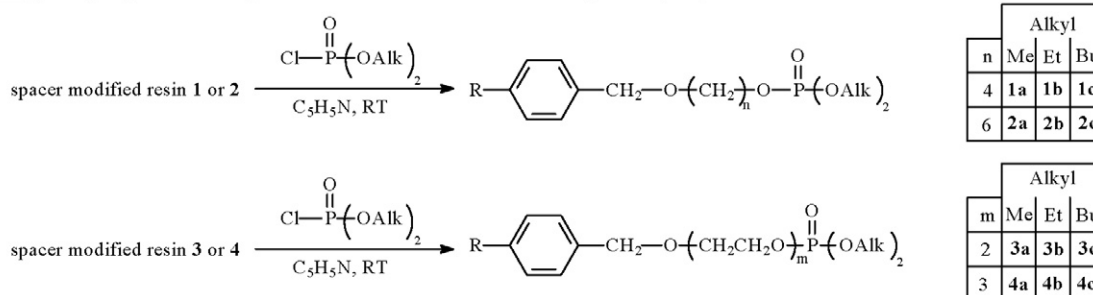
In the literature [36,50,51], the range of expectation of the P=O stretching vibration is between 1300 and 960 cm<sup>-1</sup> and P–O–C stretching vibrations bands are found between 1260 and 855 cm<sup>-1</sup>.

In the phosphorylated polymer **2c** (see Fig. 1), the P=O band appears at 1212 cm<sup>-1</sup> and the P–O–C band shows at 1026 cm<sup>-1</sup>. Both stretching vibrations are broad. The P=O band for the resins **2a** and **2b** appears at 1218 cm<sup>-1</sup> and 1212 cm<sup>-1</sup>, whereas the P–O–C band is centred at 1026 cm<sup>-1</sup> and 1027 cm<sup>-1</sup>, respectively. Additionally the intensive double band at 836 cm<sup>-1</sup>/823 cm<sup>-1</sup> of the modified resin **2** decreases in all three resins and a new weaker band appears. For **2a**, this band shows at 856 cm<sup>-1</sup>, for **2b** and **2c** at 860 cm<sup>-1</sup> and 859 cm<sup>-1</sup>, respectively. For the phosphorylated resins **1a–c**, **3a–c** and **4a–c**, the stretching vibration of the P=O group appears at higher wave numbers around 1270 cm<sup>-1</sup>. The broad P–O–C band in contrast is centred at 1027 cm<sup>-1</sup>.

1st step: Modification of the merrifield resin with different diols



2nd step: Phosphorylation of the spacer modified resins with different dialkyl chlorophosphates



Scheme 1. Synthesis of different trialkyl phosphate resins in a two-step reaction.

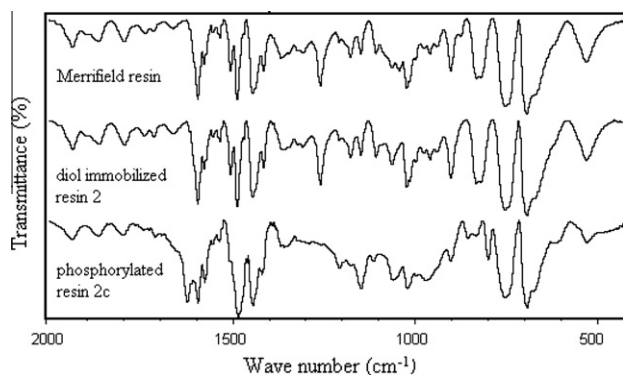


Fig. 1. Transmittance FT-IR spectra of the Merrifield resin, the 6-hydroxyhexoxy modified resin **2** and the dibutyl-(hexane-1,6-diyl) phosphate resins **2c**.

Table 1  
Characteristic FT-IR bands of the spacer modified resins 1–4.

Resin	$\bar{\nu}_{(\text{O}-\text{H})}$ ( $\text{cm}^{-1}$ )	$\bar{\nu}_{(\text{C}-\text{O})}$ ( $\text{cm}^{-1}$ )	$\bar{\nu}_{(\text{C}-\text{O})}$ ( $\text{cm}^{-1}$ )
1	3436	1091	1027
2	3441	1264	1027
3	3433	1088	1048
4	3457	1093	1029

### 3.2. Extraction experiments in single component system: Pt(IV)

#### 3.2.1. Equilibration study and determination of the capacity

The extraction of Pt(IV) using different synthesised resins in aqueous acidic solutions (at a pH value of 1.43) is shown in Fig. 2. Some of the trialkyl phosphate modified solid supports exhibits excellent extraction properties, for example the dialkyl-(hexane-1,6-diyl) phosphate resins **2a–2c**. The equilibrium is already established within 15 min when platinum is brought into contact with these resins. In the case of the dibutyl-(butane-1,4-diyl) phosphate resin **1c**, the equilibrium is reached after 60 min.

30% of the metal was extracted with dialkyl-(butane-1,4-diyl) phosphate resins **1a** and **1b**. The extraction of Pt(IV) did not exceed 50% and 10% when using dialkyl-(3-oxapentane-1,5-diyl) phosphate resins **3a** and **3b–3c** and 20% in the case of the dialkyl-(3,6-dioxaoctane-1,8-diyl) phosphate resins **4a–4c**, respectively. The Merrifield resin itself and the spacer modified resins **1–4** exhibit no extraction of platinum. Thus, there is an apparent need to use the phosphorylated polymers **1c** and **2a–2c** for further extraction experiments.

The capacity of the resins was determined with the help of recurring batch extraction experiments. During this procedure, the resin gets repeatedly into contact with 5 mL of a fresh Pt solution, which is measured prior to and after the experiment. The extraction ability of dialkyl-(hexane-1,6-diyl) phosphate resins **2a**, **2b** and **2c** remains constant for 42, 43 and 25 extraction steps, respectively, and then decreases slowly (Fig. 3). After 67 extraction steps for **2a** and **2b** and 55 for **2c**, the maximum extraction is reached. The capacity was calculated according to Eq. (2) and found to be  $113.08 \text{ mg g}^{-1}$  ( $0.580 \text{ mmol g}^{-1}$ ),  $118.27 \text{ mg g}^{-1}$  ( $0.606 \text{ mmol g}^{-1}$ ) and  $85.38 \text{ mg g}^{-1}$  ( $0.438 \text{ mmol g}^{-1}$ ) for **2a**, **2b** and **2c**, respectively. In contrast, the maximum extraction of the dibutyl-(butane-1,4-diyl) phosphate resin **1c** was reached after only 5 extraction steps with an extraction capacity of  $3.89 \text{ mg g}^{-1}$  ( $0.020 \text{ mmol g}^{-1}$ ). The comparison of these data shows the excellent extraction capacities of the dialkyl-(hexane-1,6-diyl) phosphate resins **2a–2c** for the extraction of Pt(IV) from aqueous acidic solutions. Hence, only these three resins were used for the following studies.

#### 3.2.2. Effect of hydrochloric acid concentration

PGM are normally leached out of spent catalytic converters with the help of strong oxidising acidic solutions, for example HCl/H<sub>2</sub>O<sub>2</sub> or aqua regia [4,52–54]. In these solutions, the chloride ions act as complexing agents which results in the formation of hexachloroplatinate(IV). For this reason, it is important to determine the effect of hydrochloric acid on the extraction of Pt(IV). As can be seen in Fig. 4, the extraction remains constantly high for all the resins

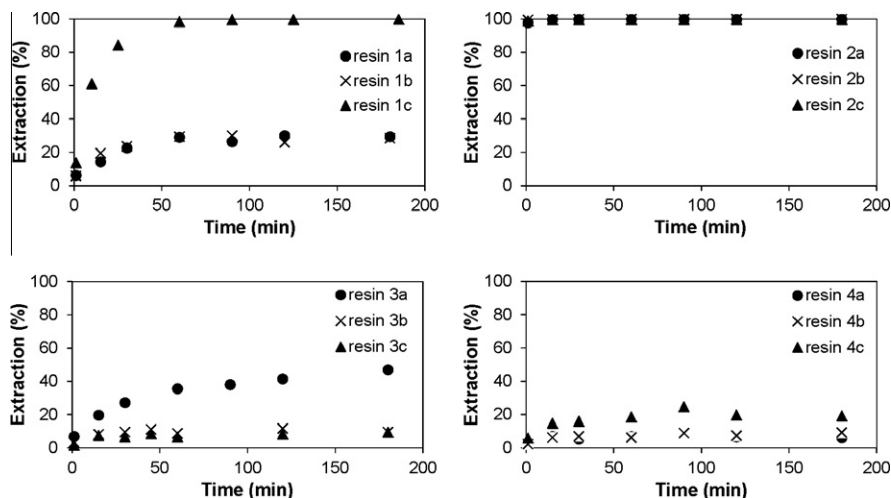


Fig. 2. Establishment of equilibrium for the extraction of Pt(IV) in aqueous acidic solutions from different trialkyl phosphate modified resins ( $10^{-4}$  mol L $^{-1}$  Pt solution in 0.039 mol L $^{-1}$  hydrochloric acid).

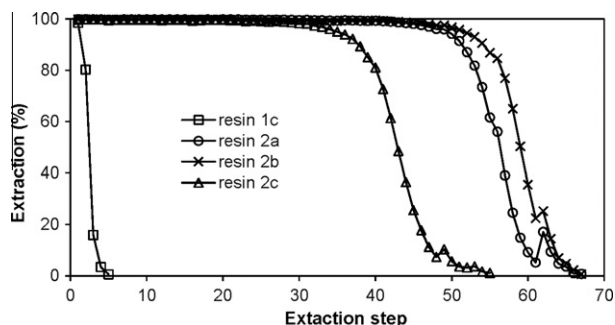


Fig. 3. Recurring batch extraction of Pt(IV) in aqueous acidic solutions ( $10^{-4}$  mol L $^{-1}$  Pt solution in 0.039 mol L $^{-1}$  hydrochloric acid).

**2a–2c** in 1 mol L $^{-1}$  HCl and decreases slightly at higher concentrations. In 8 mol L $^{-1}$  hydrochloric acid, 93% of the platinum are still extracted with **2c** and 91% with the other two polymers.

The decrease of platinum extraction with increasing hydrochloric acid concentration correlates with the increasing concentration of chloride ions. These counter ions compete with the platinum anions for the binding places at the resin.

### 3.2.3. Effect of temperature and concentration

In Table 2, the results of the extraction behaviour at different temperatures are presented for the resin **2c**. The determination

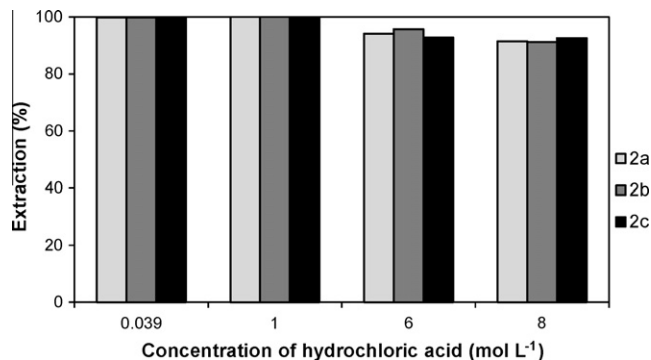


Fig. 4. Extraction of Pt(IV) in various aqueous acidic solutions ( $10^{-4}$  mol L $^{-1}$  Pt solution).

was done at different metal concentrations while the hydrochloric acid concentration was held constant. The extraction yield increases with increasing temperature (from 10 °C to room temperature) and decreases when the temperature is further enhanced up to 30 °C and 40 °C. It can be concluded for all three concentrations of Pt(IV) that there is only a slight dependence of the extraction on the temperature. In addition, the extraction of platinum is at 98% even when the metal and the chloride ion concentration are increased. Hence, the competition is exacerbated.

### 3.2.4. Adsorption isotherms

The equilibration data obtained in Section 3.2.3 was mathematically analysed with two adsorption isotherm models, namely Langmuir and Freundlich, according to the procedure described by Zargaran and co-worker [55].

The Langmuir isotherm is based on different approaches: firstly, there is a monolayer coverage of the molecules adsorbed on the surface, and secondly, the maximum adsorption corresponds to the monolayer. The whole surface is uniform and there are no interactions between the adsorbed molecules or migration. According to Eq. (6),  $c_e/q_e$  is plotted against  $c_e$  (see Fig. 5) and the Langmuir constants  $q_m$  and  $K_L$  are available through the slope and intercept, respectively.

The empirical based Freundlich isotherm assumes a heterogeneous surface and no maximum adsorption. Using Eq. (8), a plot of  $\ln q_e$  against  $\ln c_e$  results in a straight line with  $n$  and  $K_F$ , accessible through the slope and intercept as can be seen from Fig. 6.

The results and the correlation coefficients for the Langmuir and Freundlich isotherms are presented in Table 3. The Langmuir constant  $K_L$  decreases with increasing temperature. The higher the value of this constant, the stronger is the affinity of the resin to bind the metal ion. This correlates with the Freundlich constant  $n$  describing the preference of the adsorption that also decreases

Table 2

Extraction yields for batch experiments with the dibutyl-(hexane-1,6-diyl) phosphate resin **2c** at varying Pt(IV) concentrations and different temperatures (hydrochloric acid concentration is constant at 4.5 mol L $^{-1}$ ).

$c$ (mol L $^{-1}$ )	10 °C $E$ (%)	22 °C $E$ (%)	30 °C $E$ (%)	40 °C $E$ (%)
0.0001	98.6	99.5	98.4	97.9
0.0005	98.4	98.5	98.1	97.8
0.001	98.1	98.1	97.7	97.6

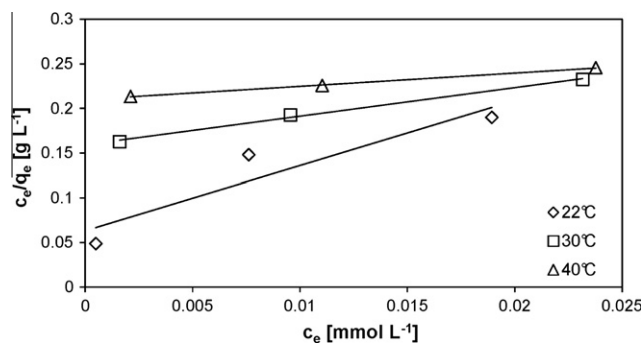


Fig. 5. Plot of Langmuir isotherm at different temperatures for the extraction of Pt(IV) with dibutyl-(hexane-1,6-diyl) phosphate resin **2c**.

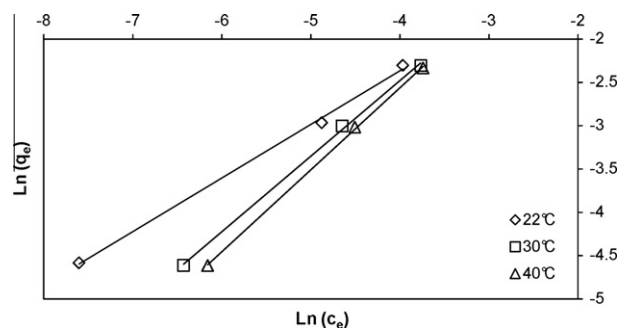


Fig. 6. Plot of Freundlich isotherm at different temperatures for the extraction of Pt(IV) with dibutyl-(hexane-1,6-diyl) phosphate resin **2c**.

**Table 3**  
Langmuir and Freundlich isotherm constants for Pt(IV) extraction on the dibutyl-(hexane-1,6-diyl) phosphate resin **2c** at different temperatures.

T (°C)	Langmuir			Freundlich		
	$K_L$ (L mmol <sup>-1</sup> )	$q_m$ (mmol g <sup>-1</sup> )	$R^2$	$n$	$K_F$	$R^2$
22	115.4802	0.1372	0.8753	1.6166	1.1134	0.9981
30	20.1187	0.3122	0.9955	1.1471	2.7363	0.9989
40	7.0877	0.6725	0.9989	1.0572	3.3865	0.9996

with enhanced temperature. These tendencies are in accordance with the extraction yield demonstrated in Table 2 (compare with Section 3.2.3 of the text). The Langmuir constant  $q_m$  and the Freundlich constant  $K_F$  are referring to the adsorption capacity. In both isotherm models, the same trend appears. The adsorption values increase with higher temperatures.

In general, the application of these isotherms on ion exchange processes is extensively discussed in the literature. There are two contrary opinions on this topic. On the one hand, the usage of the isotherms is refused due to the continuous development and better understanding in the field of ion exchange. Subsequently, the isotherms seemed to be antiquated [56]. On the other hand, the isotherms present a possibility to simplify complex processes and can lead to useful results [55,57]. Some remarks are given by Misak [58,59] with respect to the Langmuir isotherm, for example that the concentration of one of the ions has to be kept constant.

### 3.2.5. Thermodynamic parameters

The procedure described by Zargaran and co-worker [55] was used for the determination of the thermodynamic parameters. The standard free energy  $\Delta G^0$  was calculated according to Eq. (9). In order to determine the enthalpy  $\Delta H^0$  and the entropy  $\Delta S^0$ , a plot

of  $\ln K_F$  against  $1/T$  was used, resulting in a straight line with the slope, referring to the enthalpy and the intercept related to the entropy. The results are presented in Table 4. The negative standard free energy corresponds to a spontaneous reaction and a feasible process. The value of the enthalpy is also negative. This is due to an exothermic sorption of the metal to the resin. The negative entropy is related to a lower randomness tendency.

### 3.2.6. Elution

An important characteristic of the separation process is the possibility to elute the extracted metal from the resin. One of the commonly used stripping agents in SX and SPE is an acidic thiourea (tu) solution [27,29,31,33,41].

The recovery of the platinum was determined with a 0.5 mol L<sup>-1</sup> thiourea solution in 0.1 mol L<sup>-1</sup> hydrochloric acid. Yields between 76% for the dialkyl-(hexane-1,6-diyl) phosphate resin **2c** and 80% for the other two resins were achieved (Fig. 7). Warshawsky [60] and Kovacheva and Djingova [61] discussed the back extraction as a nucleophilic attack of the thiourea ligand on the metal. This results in the formation of a cationic thiourea complex with the composition [Pt(tu)<sub>4</sub>]<sup>2+</sup>. The platinum(IV) is reduced to platinum(II) [62,63] and the thiourea ligand is oxidised to formamidine disulphide [62,64].

### 3.3. Extraction experiments in binary systems

#### 3.3.1. Selectivity of Pt(IV) towards Pd(II)

The selectivity of the resins for Pt(IV) and Pd(II) was determined using various two-component solutions with different metal and acid concentration. As can be concluded from Table 5, the platinum and palladium extraction hardly changes when the metal concentration is enhanced by the factor of five. When the solution is furthermore modified to higher HCl concentrations, the extraction yield of palladium dropped to less than half of the previous value for the dibutyl-(hexane-1,6-diyl) phosphate resin **2c**, and to two-thirds for the dialkyl-(hexane-1,6-diyl) phosphate resins **2a** and

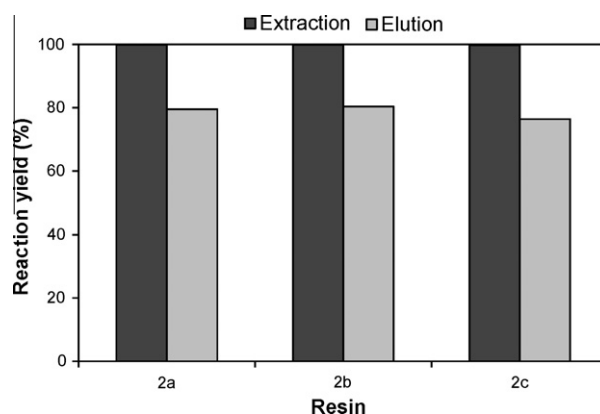


Fig. 7. Extraction and elution of Pt(IV) from different dialkyl-(hexane-1,6-diyl) phosphate resins (extraction with  $2.5 \times 10^{-4}$  mol L<sup>-1</sup> metal solution in 0.097 mol L<sup>-1</sup> hydrochloric acid; stripping with 0.5 mol L<sup>-1</sup> thiourea solution in 0.1 mol L<sup>-1</sup> hydrochloric acid).

**Table 4**

Thermodynamic parameters  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$  for Pt(IV) extraction on the dibutyl-(hexane-1,6-diyl) phosphate resin **2c** at different temperatures.

T (°C)	$\Delta G^0$ (kJ mol <sup>-1</sup> )	$\Delta H^0$ (kJ mol <sup>-1</sup> )	$\Delta S^0$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$R^2$
22	-11.65	-1.71	-5.23	0.9636
30	-7.56			
40	-5.10			

**Table 5**

Extraction yield and separation factor for batch experiments of Pt(IV) and Pd(II) in solutions with varying metal and acid concentration.

Resin	Solution	$E_{\text{Pt}}$ (%)	$S_{\text{Pd}}^{\text{Pt}}$	$E_{\text{Pd}}$ (%)	$S_{\text{Pt}}^{\text{Pd}}$
<b>2a</b>	1	99.9	1.86	99.8	0.54
	2	99.9	10	99.6	0.10
	3	97.8	22	66.6	0.04
<b>2b</b>	1	99.9	7.33	99.3	0.14
	2	99.9	8.81	99.7	0.11
	3	98.2	24	69.3	0.04
<b>2c</b>	1	99.8	2.05	99.6	0.39
	2	99.8	11	98.4	0.09
	3	92.9	17	43.7	0.06

Solution 1:  $c_{\text{Metal}} = 10^{-4} \text{ mol L}^{-1}$ ,  $c_{\text{HCl}} = 0.054 \text{ mol L}^{-1}$ .

Solution 2:  $c_{\text{Metal}} = 5 \times 10^{-4} \text{ mol L}^{-1}$ ,  $c_{\text{HCl}} = 0.270 \text{ mol L}^{-1}$ .

Solution 3:  $c_{\text{Metal}} = 5 \times 10^{-4} \text{ mol L}^{-1}$ ,  $c_{\text{HCl}} = 4.500 \text{ mol L}^{-1}$ .

**2b.** In contrast, platinum extraction decreases by 7% for **2c**, and 2% for **2a** and **2b**.

There are two effects explaining this behaviour. On the one hand, the negatively charged Pt(IV) and Pd(II) anions are in competition with each other. As long as there are enough binding places, the extraction for both metals is good. If the hydrochloric acid concentration is increased as well, the extraction of platinum and palladium decreases due to the excess of competing chloride ions. On the other hand, there is a difference in the tendency to form ion pairs with anion exchangers [9,47]. In comparison to metal ions with a lower charge density, metal ions with a higher charge density (defined as the ratio between charge and size) do not form ion pairs so easily. Bernardis and co-worker [9] explain this as a result of the size of the hydration shell that is encircling the ion itself. The bigger the hydration shell (and the higher the charge density), the lesser is the interdependency with the counter-ion coulomb interaction and the lesser is the extraction with the anion exchanger.

Another fact that needs to be considered is the speciation of platinum and palladium in different acidic media. Palladium(II) exists mainly in the form of  $[\text{PdCl}_3(\text{H}_2\text{O})]^-$  and  $[\text{PdCl}_4]^{2-}$  in aqueous acidic solutions [38b,65,66]. Both species are present in solutions with chloride concentrations between  $0.1 \text{ mol L}^{-1}$  and  $0.5 \text{ mol L}^{-1}$  [65]. Kasaini and co-worker [38b] showed that  $[\text{PdCl}_3(\text{H}_2\text{O})]^-$  is the predominant species at concentrations of chloride ions of  $0.01 \text{ mol L}^{-1}$ . At higher  $\text{Cl}^-$  concentration (more than  $1 \text{ mol L}^{-1}$  [65] and  $2 \text{ mol L}^{-1}$  [38b]), tetrachloropalladate(II) is the dominant species.

In the case of platinum(IV), the literature and the associated data is not so clear. Most sources agree in the fact that at low pH values and depending on the chloride content, different ratios of  $[\text{PtCl}_6]^{2-}$  and  $[\text{PtCl}_5(\text{H}_2\text{O})]^-$  occur in solutions. It seems to be the consensus that the lower the  $\text{Cl}^-$  concentration is, the more the  $[\text{PtCl}_5(\text{H}_2\text{O})]^-$  species gets predominant [65,67–69].

In summary, the phosphorylated polymers **2a–2c** exhibit a high affinity to platinum(IV) over palladium(II), especially when the chloride concentration is  $4.5 \text{ mol L}^{-1}$ . This can also be seen from the separation factors in Table 5.

### 3.3.2. Selectivity of Pt(IV) towards Rh(III)

The selectivity of the resins for Pt(IV) and Rh(III) was also determined using various two-component solutions with different metal and acid concentrations. When the chloride ion concentration is increased substantially, the change in the extraction of platinum occurs (Table 6). The dibutyl-(hexane-1,6-diyl) phosphate resin **2c** extracts rhodium to 50%, while the extraction is 56% and 52% in the case of **2a** and **2b**, respectively. Yet, a slight increase in the metal ion concentration (and subsequently an enhancement of the hydrochloric acid concentration by the factor of five) results

in a drop of the extraction yield. If the concentration of the chloride ions is further increased, the extraction yield is decreased below 1% for **2c** and to 3% for **2a** and **2b**.

As discussed in the previous section of the text (compare Section 3.3.1), the negatively charged platinum and rhodium anions (mentioned below) are in competition with each other and with the chloride ions. Additionally, the influence of the charge density (and the hydration shell) results in the tendency of these complexes to be able to form ion pairs with anion exchangers, as described by Bernardis and co-worker [9]:  $[\text{MCl}_6]^{2-} > [\text{MCl}_4]^{2-} \gg [\text{MCl}_6]^{3-} > \text{aqua species}$  (M refers to the metal).

In this context, the speciation of rhodium in aqueous acidic solutions is of some importance. Platinum group metals with trivalent oxidation states are known to form a lot of different aqua chloro complexes. The predominant species in high chloride concentration (above  $6 \text{ mol L}^{-1}$ ) is  $[\text{RhCl}_6]^{3-}$  [9,47,70]. If the  $\text{Cl}^-$  concentration is decreased, the equilibrium between the different anionic rhodium complexes changes to  $[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$  as the predominant species and then to  $[\text{RhCl}_4(\text{H}_2\text{O})_2]^-$ . If the concentration of chloride ions is below  $0.1 \text{ mol L}^{-1}$ , neutral and cationic complexes are also possible [9,70].

## 3.4. Extraction experiments in ternary systems

### 3.4.1. Selectivity and temperature dependence of Pt(IV) towards Pd(II) and Rh(III)

For the three PGMs, the selectivity of the dialkyl-(hexane-1,6-diyl) phosphate resins was determined at three different temperatures with variation of the solutions. In Fig. 8, the extraction yield is illustrated on the example of **2c**. There is almost no temperature dependency of the platinum extraction. In  $10^{-4} \text{ mol L}^{-1}$  PGM solution, palladium extraction decreases barely when altering the temperature. However, increasing the metal and acid concentration leads to a different extraction behaviour. With higher temperatures palladium extraction deteriorates by 9%. In the case of rhodium, the falling extraction trend is already visible at low metal and acid concentration. The extraction yield at  $10^\circ\text{C}$  and  $25^\circ\text{C}$  is nearly constant, whereas a further increase in temperature results in the significant loss of 32% in the extraction ability. In a solution with  $5 \times 10^{-4} \text{ mol L}^{-1}$  metal and  $4.5 \text{ mol L}^{-1}$  hydrochloric acid, rhodium is hardly ever extracted.

The two other dialkyl-(hexane-1,6-diyl) phosphate resins **2a** and **2b** behave in a similar way. The separation factors were calculated and presented in Tables 7 and 8. The resin exhibits a high affinity for platinum over palladium and rhodium, especially at higher metal and acid concentrations.

### 3.5. Comparison with other extraction systems

In order to classify the capacities of the phosphorylated resins **2a**, **2b** and **2c**, they are compared with those obtained in the literature. The capacities for the solid-phase extraction of different precious metals using phosphorous containing ligands are presented in Table 9.

The resins modified with phosphine sulphide exhibit high capacities for gold and palladium depending on the kind and length of the spacer between the solid support and the ligand. Their capacities are somewhat higher compared to our results and the phosphine sulphide modified resins extract gold and palladium selectively in the presence of platinum, rhodium, iridium, iron, copper, nickel and zinc. However, these resins show very slow extraction kinetics, even if organic solvents are additionally used to increase the swelling behaviour of the solid support [33].

In contrast to that, the capacity of the tris(2,6-dimethylphenyl) phosphine modified resin, forming quarternary phosphonium chloride, is 6- to 8-fold lower in comparison to the capacities of the



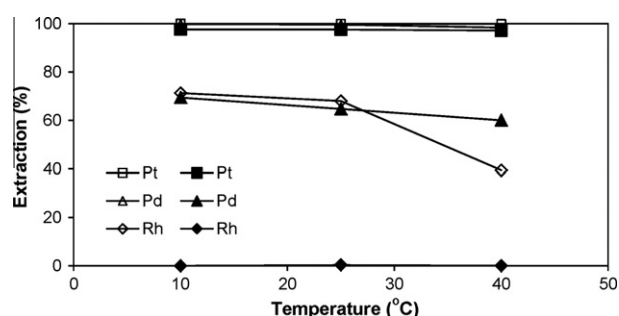
**Table 6**  
Extraction yield and separation factor for batch experiments of Pt(IV) and Rh(III) in solutions with varying metal and acid concentration.

Resin	Solution	$E_{Pt}$ (%)	$S_{Rh}^{Pt}$	$E_{Rh}$ (%)	$S_{Pt}^{Rh}$
<b>2a</b>	1	99.9	577	56.4	<0.01
	2	99.9	3398	37.7	<0.01
	3	97.8	1405	3.1	<0.01
<b>2b</b>	1	99.8	441	52.2	<0.01
	2	99.9	3855	38.6	<0.01
	3	98.3	2160	2.6	<0.01
<b>2c</b>	1	99.4	163	49.9	0.01
	2	99.8	2328	21.3	<0.01
	3	93.4	4830	0.3	<0.01

Solution 1:  $c_{Metal} = 10^{-4} \text{ mol L}^{-1}$ ,  $c_{HCl} = 0.049 \text{ mol L}^{-1}$ .

Solution 2:  $c_{Metal} = 5 \times 10^{-4} \text{ mol L}^{-1}$ ,  $c_{HCl} = 0.246 \text{ mol L}^{-1}$ .

Solution 3:  $c_{Metal} = 5 \times 10^{-4} \text{ mol L}^{-1}$ ,  $c_{HCl} = 4.500 \text{ mol L}^{-1}$ .



**Fig. 8.** Extraction of two different PGM solutions from dibutyl-(hexane-1,6-diyl) phosphate resin **2c** at different temperatures (blank symbols refer to solution with  $10^{-4} \text{ mol L}^{-1}$  metal content in  $0.064 \text{ mol L}^{-1}$  hydrochloric acid; filled symbols refer to solution with  $5 \times 10^{-4} \text{ mol L}^{-1}$  metal content in  $4.5 \text{ mol L}^{-1}$  hydrochloric acid).

resins **2a–2c**. The resin extract only Au(III) and Pt(IV) in the presence of Fe(III) and Cu(II) in low HCl concentration, but the extraction of iron is enhanced with increasing hydrochloric acid concentration due to the formation of anionic chloro complexes [35].

In comparison to the phosphate resins **2a–2c** the activated carbon pellets impregnated with dithiophosphinic and monothio-phosphoric acid exhibit similar separation factors and an extraction tendency of Pd(II) > Pt(IV) > Rh(III). Albeit the capacities of the phosphate resins **2a–2c** are 18-fold higher [38a].

The equilibrium of the phosphonium-type ionic liquids is reached within 60 min. So these materials exhibit similar kinetics for the extraction of platinum. Yet, the extraction efficiency is strongly dependent of the anion and varies between 25% and 99%. Moreover, other precious metals, for example palladium, are co-extracted from  $1\text{--}2 \text{ mol L}^{-1}$  hydrochloric acid solution [39].

**Table 7**  
Separation factor for batch experiments with varying temperature for Pt(IV), Pd(II) and Rh(III) in solution with  $10^{-4} \text{ mol L}^{-1}$  metal concentration and  $0.064 \text{ mol L}^{-1}$  hydrochloric acid.

Resin	$T$ (°C)	$S_{Pd}^{Pt}$	$S_{Rh}^{Pt}$	$S_{Rh}^{Pd}$	$S_{Pt}^{Pd}$	$S_{Pt}^{Rh}$	$S_{Pd}^{Rh}$
<b>2a</b>	10	1.00	1.38	1.38	1.00	0.72	0.72
	25	1.00	1.43	1.43	1.00	0.71	0.70
	40	1.01	2.41	2.37	0.99	0.42	0.42
<b>2b</b>	10	1.00	1.40	1.39	0.72	0.72	0.72
	25	1.00	1.45	1.45	1.00	0.69	0.69
	40	1.01	2.53	2.49	0.99	0.40	0.40
<b>2c</b>	10	1.00	1.40	1.40	1.00	0.71	0.71
	25	1.00	1.47	1.46	0.68	0.68	0.68
	40	1.02	2.54	2.507	0.98	0.39	0.40

**Table 8**  
Separation factor for batch experiments with varying temperature for Pt(IV), Pd(II) and Rh(III) in solution with  $5 \times 10^{-4} \text{ mol L}^{-1}$  metal concentration and  $4.5 \text{ mol L}^{-1}$  hydrochloric acid.

Resin	$T$ (°C)	$S_{Pd}^{Pt}$	$S_{Rh}^{Pt}$	$S_{Rh}^{Pd}$	$S_{Pt}^{Pd}$	$S_{Pt}^{Rh}$	$S_{Pd}^{Rh}$
<b>2a</b>	10	1.45	309	214	0.69	<0.01	<0.01
	25	1.51	87	57	0.66	0.01	0.02
	40	1.60	177	111	0.62	0.01	0.01
<b>2b</b>	10	1.39	n.c.	n.c.	0.72	n.c.	n.c.
	25	1.46	99	68	0.68	0.01	0.01
	40	1.56	n.c.	n.c.	0.64	n.c.	n.c.
<b>2c</b>	10	1.41	n.c.	n.c.	0.71	n.c.	n.c.
	25	1.51	303	201	0.66	<0.01	<0.01
	40	1.62	1931	1193	0.62	<0.01	<0.01

n.c.: Not calculated due to no measurable rhodium extraction.

**Table 9**

Comparison of the capacities given in the literature for the solid-phase extraction of precious metals with phosphorous containing ligands.

Extraction	Solid support	$q_e$ (mmol g <sup>-1</sup> )				Reference
		Au(III)	Pt(IV)	Pd(II)	Rh(III)	
Dimethyl-(hexane-1,6-diyl) phosphate	MR <sup>a</sup>		0.580			This work
Diethyl-(hexane-1,6-diyl) phosphate			0.606			
Dibutyl-(hexane-1,6-diyl) phosphate				0.438		
Phosphine sulphide	MR <sup>a</sup>	0.4–6.5		0.11–0.72		[33]
Quart. phosphonium chloride	PS <sup>b</sup>	0.08	0.075			[35]
Bis(2,4,4-trimethylpentyl) dithiophosphinic acid	ACP <sup>c</sup>		0.033	0.07	0.005	[38a]
Bis(3-ethylhexyl) monothiophosphoric acid			0.032	0.115	0.005	

<sup>a</sup> Merrifield resin.<sup>b</sup> Chloromethylated polystyrene.<sup>c</sup> Activated carbon pellets.

#### 4. Conclusion

In this paper, the synthesis of SPE resins based on trialkyl phosphate which was covalently bound to Merrifield solid support via different diol spacers, were shown. The systematic change in the kind and length of the spacer leads to the phosphorylated polymers **2a–2c** bearing dialkyl-(hexane-1,6-diyl) phosphate groups which possess excellent extraction properties towards precious metals like platinum, and good extraction abilities with regards to palladium and rhodium. In order to improve the extraction behaviour (especially) of platinum(IV), a systematical investigation of mono, binary and ternary metal compositions was done. Optimal conditions for the separation of platinum from the other two noble metals were found taking into account the hydrochloric acid concentration and the temperature.

Due to the different species of the PGMs in varying compositions of the aqueous acidic solution and also the tendency of the metals to undergo ligand substitution reactions, two possible mechanisms for the extraction can be used as an explanation. Platinum is known to exhibit slow ligand substitution kinetics as it is relatively inert in comparison to palladium which is more labile and shows fast ligand substitution kinetics. On the other hand, platinum favours the formation of ion pairs due to a lower charge density whereas palladium, with its bigger hydration shell, has got a lesser interdependency with the counterion and therefore, the extraction via ion pair formation is preferred to a lesser extent.

Trialkyl phosphates are described to be able to protonate on the phosphoryl oxygen [71,72], so the ion exchange is the favoured extraction mechanism, especially when the hydrochloric acid is raised.

The dependency of the precious metal extraction on acid concentration and temperature can be exploited and summarised in two different extraction tendencies. When the hydrochloric acid concentration is low, platinum and palladium are extracted to the same extent in accordance with the tendency: Pt(IV)  $\approx$  Pd(II) > Rh(III). Increasing the acid concentration results in a change of the extraction tendency to Pt(IV) > Pd(II)  $\gg$  Rh(III).

In comparison to other SPE systems with phosphorous containing ligands [33,35,38a] the dialkyl-(hexane-1,6-diyl) phosphate resins **2a–2c** exhibits excellent capacities for platinum. In batch experiments, the resins **2a–2c** demonstrated their extraction preferences and selectivity towards platinum, especially in strong hydrochloric acid media. In addition to the selectivity the capacities and elution with acidic thiourea solution offers promising prospects for the application of these extracting agents in column experiments. Therefore, the extraction behaviour towards a process solution obtained by leaching spent automotive catalytic converter with aqua regia would be the next step for research.

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