

A new ^{17}O -isotopic enrichment method for the NMR characterisation of phosphate compounds

Alexandrine Flambard, Lionel Montagne* and Laurent Delevoye

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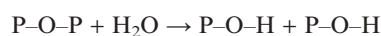
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Heating phosphate compounds under ^{17}O -enriched water vapour is an easy and rapid method to prepare homogeneously enriched and pure samples for the acquisition of ^{17}O NMR spectra with a good sensitivity.

Although its low natural abundance requires isotopic enrichment, solid-state NMR spectroscopy of oxygen-17 is commonly used for the structural study of a wide range of oxide materials like glasses, gels, catalysts and ionic conductors.^{1–4} Phosphate compounds are found in all of these materials,^{5–8} and they are also widely used as additives in food, pharmaceutical and agricultural domains.^{9–11} However, although there is a large number of publications on solid-state ^{31}P NMR spectroscopy,^{12–18} ^{17}O solid-state NMR studies of phosphate compounds are not numerous.^{19–22} This is due mainly to the fact that the conventional ^{17}O -isotopic enrichment method of oxide compounds, which is based on the hydrolysis of a MCl_x salt by ^{17}O -enriched water,²³ is not easy to apply to phosphates. The preparation of ^{17}O -enriched alumina was recently reported²⁴ using a hydrothermal method, but its applicability to phosphate compounds is not possible because it involves a metallic precursor.

In the case of ^{17}O -enrichment using the hydrolysis of PCl_5 , we have shown¹⁹ that a careful experimental procedure must be used to limit the presence of residual hydroxyl groups and to obtain pure phases. Glassy ^{17}O -enriched sodium metaphosphate (NaPO_3) was prepared¹⁹ by the hydrolysis of PCl_5 , and other sodium phosphate¹⁹ and borophosphate²⁰ glass compositions were derived by melting the metaphosphate with the appropriate additives [*e.g.* $(\text{NH}_4)_2\text{HPO}_4$, Na_2CO_3 , B_2O_3]. This procedure has, however, several major drawbacks: (1) the enriched glasses have a lower level of ^{17}O -enrichment than the initial product NaPO_3 , (2) the procedure is long and delicate and (3) the available glass compositions are limited since they must contain sodium and should be derived from NaPO_3 . An alternative method²¹ consists in the thermal oxidation of red phosphorus into P_2O_5 , but strict dry conditions must be used to obtain a pure enriched compound, and the handling of P_2O_5 as a precursor of phosphates is not easy owing to its strong hygroscopicity. An oxygen exchange between phosphate ions and water would be possible in solution, but it is reported²⁵ that the process is very slow and some hydrolysis of POP groups may occur. Thus, there is a large need for an alternative isotopic enrichment method that would be easier, more versatile, and faster than using PCl_5 hydrolysis or P thermal oxidation.

Phosphates are hydrolysed by water in the liquid or in the vapour²⁶ state, leading to the formation of P–OH groups:



These P–OH groups can then be condensed by a thermal treatment above 300 °C, which leads to the enriched phosphate, provided that the reaction time is sufficient to enable a statistical exchange between the oxygens:



Hence, we prepared ^{17}O -enriched phosphate compounds by a treatment under ^{17}O -enriched water vapour, at a temperature close to 600 °C, at which temperature the hydrolysis and condensation kinetics are very fast. This method is similar to that used for ^{18}O enrichment of samples for mass spectrometry.²⁷ In this case though, the aim is to measure diffusion coefficients and the homogeneity is therefore not a relevant parameter. The efficiency of this enrichment technique is demonstrated here in a solid-state NMR study of two phosphate compounds: the sodium metaphosphate (NaPO_3) and the sodium tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$), which have different degrees of polymerisation. These sodium phosphates were chosen because (1) their structure is well known and (2) the sodium salts are somewhat hygroscopic, hence they should be sensitive to a possible incomplete hydrolysis–condensation process. The aim was to show that the ^{17}O -isotopic enrichment is homogeneous, without the formation of residual hydroxyl groups, and that the enrichment treatment does not alter the phosphate network.

The enrichment procedure consisted in heating the phosphate compound in a platinum crucible at a temperature between 500 and 700 °C. The ^{17}O -enriched water vapour (*ca.* 40 atom%) was then introduced with a partial pressure fixed by an external water bath. It should be noticed that several samples could be enriched simultaneously by introducing several platinum crucibles in the furnace. After treatment, the water vapour was collected by condensation into a liquid nitrogen trap. Heating tapes were used in order to prevent water condensation on the parts outside the furnace. The samples presented here were ^{17}O -enriched by heating NaPO_3 and $\text{Na}_5\text{P}_3\text{O}_{10}$ glasses at 550 or 700 °C, for 8 to 16 hours, using 1.0 g of 37.9% ^{17}O -enriched water. After the treatment, NaPO_3 and $\text{Na}_5\text{P}_3\text{O}_{10}$ were crystallised since the temperature used (550 or 700 °C) is above the crystallisation temperature of the glasses. The glasses were finally obtained by a further thermal treatment under air at 800 °C for 15 min and 1000 °C for 2 h for the metaphosphate and tripolyphosphate, respectively, followed by a quenching to room temperature (no loss of ^{17}O was observed after several melting treatments).

UCCS, Unité de Catalyse et Chimie du Solide, UMR-CNRS 8181, Ecole Nationale Supérieure de Chimie de Lille, Université des Sciences et Technologies de Lille, BP90108, 59655 Villeneuve d'Ascq, France.
E-mail: lionel.montagne@univ-lille1.fr

^{31}P NMR spectra (Fig. 1) of the ^{17}O -enriched and reference (non-enriched) glasses were recorded in order to verify the integrities of the phosphate networks after the enrichment treatment. Sodium phosphate glasses are good candidates since the different Q^n sites are well resolved on the ^{31}P MAS-NMR spectra.²⁸ The ^{31}P MAS-NMR spectrum of the non-enriched NaPO_3 glass [Fig. 1A(a)] shows a main resonance at -20 ppm, attributed to $Q^2(\text{Na})$ sites²⁸ and two weak resonances at -8 and $+1$ ppm due to $Q^1(\text{OH})$ and $Q^1(\text{Na})$, respectively.¹⁹ The spectra are identical for the enriched and non-enriched glasses [Fig. 1A(a) and 1B(a)], and the relative concentration of Q^1 sites is kept small for both glasses (*ca.* 0.9 mol%). We thus conclude that the enrichment treatment did not affect the structure of the metaphosphate network. The ^{31}P MAS-NMR spectra of the non-enriched (Fig. 1C) and ^{17}O -enriched (Fig. 1D) $\text{Na}_5\text{P}_3\text{O}_{10}$ glasses show the expected resonances of $Q^1(\text{Na})$ sites at $+1.4$ ppm and $Q^2(\text{Na})$ at -14.4 ppm.²⁸ Again, the quantification of the relative amount of these sites leads to identical results for ^{17}O -enriched and non-enriched glasses (62% Q^1 , 38% Q^2).

In a second step, $\{^1\text{H}\}$ - ^{31}P CP-MAS experiments have been performed in order to highlight the presence of hydroxyl groups in the NaPO_3 glasses. For the ^{17}O -enriched NaPO_3 , the comparison of the ^{31}P and $\{^1\text{H}\}$ - ^{31}P CP-MAS NMR spectra [Fig. 1B(a and b)] shows resonances at $+2$, -8 and -20 ppm, which stem from P-OH groups or adsorbed H_2O molecules, located on Q^0 , Q^1 and Q^2 sites, respectively.²⁹ Although the quantification of CP-MAS NMR spectra is not straightforward, we observe that the quantity of phosphorus sites close to protons is very low in the reference glass as well as in the enriched glass. Thus, we conclude that the treatment under water vapour does not increase the amount of hydroxyl groups in the glass.

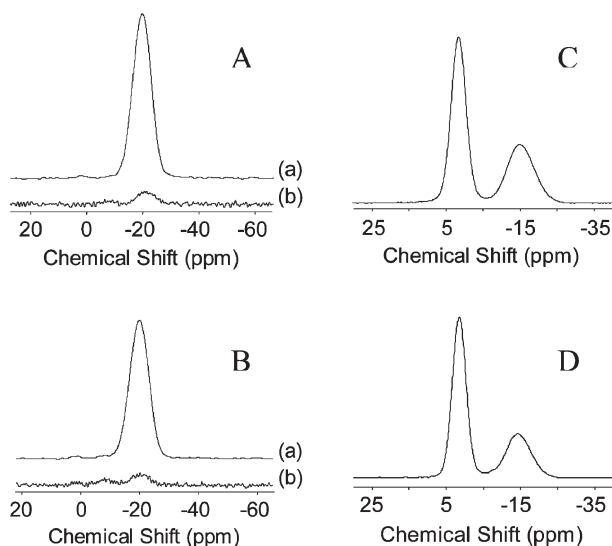


Fig. 1 ^{31}P MAS-NMR spectra of the reference (non-enriched) NaPO_3 glass (A, a), ^{17}O -enriched NaPO_3 glass (B, a), non-enriched $\text{Na}_5\text{P}_3\text{O}_{10}$ glass (C) and ^{17}O -enriched $\text{Na}_5\text{P}_3\text{O}_{10}$ glass (D). $\{^1\text{H}\}$ - ^{31}P CP-MAS NMR spectra of the non-enriched NaPO_3 glass (A, b) and ^{17}O -enriched NaPO_3 glass (B, b). They were acquired at 9.4 T, at a rotor spinning speed of 10 kHz, a $\pi/9$ pulse angle and a recycling delay of 120 s. $\{^1\text{H}\}$ - ^{31}P CP-MAS NMR spectra were recorded with a RF field of 55 kHz. The contact time was set to 1 ms.

The ^{17}O MAS-NMR spectra (Fig. 2) of the ^{17}O -enriched glasses were recorded at 18.8 T. Indeed, we have shown that the large quadrupolar broadening of the POP bridging oxygens can only be reduced at a high static magnetic field.¹⁹ Under these conditions, it is possible to quantify the relative amounts of P-O-P (bridging oxygens, BO) and P-O-Na (non-bridging oxygens, NBO) sites using the one-dimensional ^{17}O MAS-NMR spectrum, with no need to acquire a high-resolution 2D MQ-MAS spectrum, which is more difficult to quantify. The deconvolution of the ^{17}O MAS-NMR spectra of the NaPO_3 and $\text{Na}_5\text{P}_3\text{O}_{10}$ glasses is shown in Fig. 2(a and b), and the fit parameters are reported in Table 1. They were performed with the DM-fit software.³⁰ The calculated BO/NBO ratios were deduced from the relative quantities of Q^n sites measured by the decomposition of the ^{31}P NMR spectra.¹⁹ The measured BO/NBO ratios are in full agreement with the calculated values for the sodium metaphosphate (NaPO_3) and tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$), and they are identical for enriched and non-enriched samples. Thus, ^{17}O NMR spectroscopy shows that the ^{17}O isotopic enrichment method with water vapour leads to homogeneously enriched samples.

In order to address the question of the sensitivity of the method, we compared the ^{17}O MAS-NMR spectrum of the NaPO_3 glass enriched under water vapour with that obtained by the PCl_5 hydrolysis method.¹⁹ Moreover, different experimental conditions were carried out for the enrichment under water vapour: the exchange time at 550 °C was 8 or 16 h, and the temperature of the exchange was set to 550 or 700 °C (for 8 h). One can note that

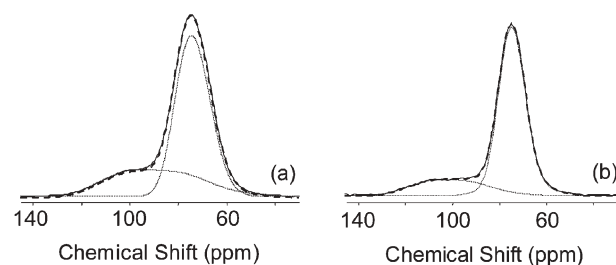


Fig. 2 ^{17}O MAS-NMR spectra of the ^{17}O -enriched NaPO_3 (a) and $\text{Na}_5\text{P}_3\text{O}_{10}$ (b) glasses, acquired at 18.8 T, at a rotor spinning speed of 30 kHz, using a recycling delay of 1 s. The total acquisition time was 20 min and 2 h for NaPO_3 and $\text{Na}_5\text{P}_3\text{O}_{10}$ respectively.

Table 1 Parameters resulting from the deconvolution of ^{17}O MAS-NMR spectra of NaPO_3 and $\text{Na}_5\text{P}_3\text{O}_{10}$: isotropic chemical shift (δ_{iso}), quadrupolar parameters (C_Q , η) and fractions of bridging (BO) and non-bridging (NBO) oxygens

Glasses	NaPO_3	$\text{Na}_5\text{P}_3\text{O}_{10}$
NBO site		
$\delta_{\text{iso}} \pm 2/\text{ppm}$	83	81
$C_Q \pm 0.1/\text{MHz}$	4.2	3.8
$\eta \pm 0.01$	0.18	0.20
Exp. NBO fraction ± 0.7 (%)	66.5	79.7
Calc. NBO fraction (%)	66.7	79.5
BO site		
$\delta_{\text{iso}} \pm 2/\text{ppm}$	119	125
$C_Q \pm 0.3/\text{MHz}$	7.6	6.8
$\eta \pm 0.01$	0.35	0.46
Exp. BO fraction ± 0.7 (%)	33.5	20.3
Calc. BO fraction (%)	33.3	20.5
Exp. BO/NBO ratio ± 0.01	0.50	0.26
Calc. BO/NBO ratio	0.50	0.26

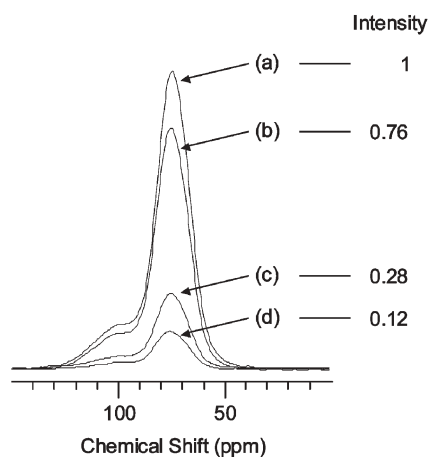


Fig. 3 ^{17}O MAS-NMR spectra of the NaPO_3 glass, ^{17}O -enriched by PCl_5 hydrolysis (a) and under H_2^{17}O vapour at 700°C for 8 h (b), 550°C for 16 h (c) and 8 h (d). The spectra were acquired at 18.8 T, at a rotor spinning speed of 20 kHz, using a recycling delay of 2 s. The total acquisition time was 20 min for each spectrum.

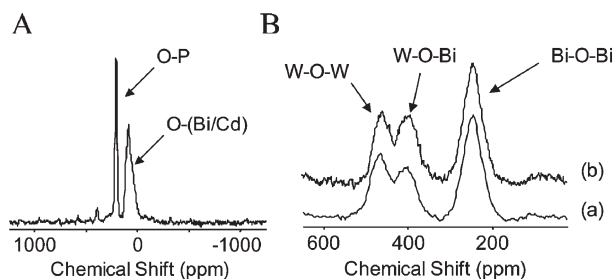


Fig. 4 ^{17}O MAS-NMR (9.4 T) spectra of A BiCd_2PO_6 (total acquisition time 512 s), and B $\text{Bi}_2\text{W}_{0.9}\text{Nb}_{0.1}\text{O}_{5.95}$ (total acquisition time 1024 s), enriched under water vapour 8 h at 650°C (a). $\text{Bi}_2\text{W}_{0.9}\text{Nb}_{0.1}\text{O}_{5.95}$ was also enriched under $^{17}\text{O}_2$ gas (20 atom%) at 700°C for 3 days (b).

NaPO_3 is melted at 700°C ($T_{\text{melting}} = 630^\circ\text{C}$). Fig. 3 compares the intensities of the four ^{17}O MAS-NMR spectra. The most intense spectrum corresponds to the glass enriched by the hydrolysis of PCl_5 [Fig. 3(a)]. Its intensity is however quasi-similar to the spectrum of the sample enriched under water vapour at 700°C for 8 h [Fig. 3(b)]. When the sample is enriched under water vapour at 550°C [Fig. 3(c and d)], the spectra have a lower intensity, but the intensity is proportional to the exchange time. We observe that the enrichment method with water vapour has a comparable yield than that obtained when using PCl_5 hydrolysis in the case where the exchange is carried out on a molten sample. The efficiency is reduced when the exchange is conducted on solid samples, since the diffusion is much slower.

We conclude that the method based on treatment under ^{17}O -enriched water vapour gives the means to prepare ^{17}O -enriched phosphate glasses with a good homogeneity and no structural modification. The efficiency is dependent on the treatment time and temperature, and the treatment is more efficient on molten samples. The procedure is much faster than that using PCl_5 hydrolysis (e.g. 8 h compared to 20 h), it is simpler (one step compared to 3 steps¹⁹), and several samples can be enriched in a single operation.

This enrichment method was successfully applied to more complex sodium niobophosphate glasses,¹² and on a crystalline

phosphate compound, BiCd_2PO_6 (Fig. 4A). Moreover, oxide compounds other than phosphates were also successfully enriched with this method. For instance, the compound $\text{Bi}_2\text{W}_{0.9}\text{Nb}_{0.1}\text{O}_{5.95}$ ⁴ (Fig. 4B) could be enriched under water vapour (a) with a better yield than that obtained with a treatment under ^{17}O -enriched O_2 gas (b).

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