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# Microwave driven ultraviolet photo-decomposition of organophosphate species

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**A novel beaker shaped electrodeless ultraviolet lamp, excited by the radiation of a conventional microwave oven, has been employed in the breakdown of organophosphate compounds in preparation for colorimetric phosphate determination. This new approach offers a highly rapid method of organophosphate decomposition prior to their analysis, with complete breakdown being achieved within 3 min. When evaluated using a number of inorganic and organophosphate compounds, quantitative release of phosphate from a carbon oxygen bond was achieved. Photo-oxidation of the organic triphosphate adenosine 5′-triphosphate results in the release of triphosphate that can then be broken down to three orthophosphate units by acid hydrolysis.**

## Introduction

Despite the many recent developments in instrument technology directed toward improving sample turnover, for most analyses the time-consuming operation is still normally the sample preparation. Digestion procedures employed to release the analyte from an organic matrix, to remove potentially interfering organic species, or to completely mineralize the sample (*e.g.*, for total N or P determination), are in turn often the most lengthy stage of the analytical protocol. Microwave radiation has found widespread acceptance in chemical analysis, principally as a means of heating and pressurising sample digests.[1] With the recent development of microwave excited ultraviolet lamps the applications of microwave radiation can now be extended to include photochemistry.

In analysis the decomposition of samples must be quantitative and particular care must be taken to reduce losses by volatilisation or by adsorption on the vessels used in the dissolution process. Control of contamination and losses is generally best achieved by minimizing the addition of reagents to the sample to achieve its mineralization and by minimizing the number of transfers between vessels.[2] Direct photolysis offers the potential of reagent-free sample digestion whilst photo-oxidation, assisted by the addition of simple and readily purified reagents such as hydrogen peroxide or persulfate, permits more aggressive treatments to be carried out.

Dissolved phosphate is frequently determined in studies of the aquatic environment and in waste management. Phosphate is a nutrient controlling algal growth, particularly in enclosed or poorly flushed water bodies such as lakes or rivers, and excessive levels can lead to excessive algal growth. In addition to orthophosphate, naturally occurring and anthropogenic phosphate can occur in a number of different forms, both as polymeric inorganic species and as organophosphate species. The most common means of determining phosphate is by colorimetry based on Phosphomolybdenum Blue chemistry but a core aspect of the method is that only the orthophosphate ion is measured. All other forms of phosphorus (inorganic polyphosphate and organic phosphorus compounds, for example) have first to be converted into orthophosphate by a digestive or oxidative procedure.

The colorimetric determination of phosphate can involve a complex sequence of steps resulting from the need to convert naturally occurring compounds such as glycerophosphate and adenosine 5′-triphosphate (ATP) into orthophosphate. These two compounds provide good examples of the types of problems that have to be overcome. In glycerophosphate, the phosphate entity is bound to the organic moiety by a simple C–O–P bond. Cleavage of the C–O–P bond results in the release of the required orthophosphate species that can be directly measured. In the case of ATP, however, cleavage of the C–O–P bond results in the release of triphosphate and requires subsequent hydrolysis to give three orthophosphate fragments for analysis. In the course of analysis of both of these compounds a common feature has been the cleavage of the C–O bond; a step that is commonly carried out by using ultraviolet radiation.

The breakdown of organophosphate compounds to inorganic phosphate has been carried out in a number of different ways. Chemical oxidation of the organics can be carried out batchwise using reagents such as persulfate[3–5] and by treatment with focussed microwaves.[6] Such methods have been adapted for use in continuous flow analysers using microwave[7] or more conventional heating methods.[8]

Armstrong first employed high intensity ultraviolet radiation (1200 W Hg arc lamp) to release inorganic phosphate from organophosphorus compounds.[9] Batch photochemical decomposition of organophosphorus compounds is facilitated by the addition of acidic persulfate to the samples.[10] A number of continuous flow analyser systems have been developed based on ultraviolet photolysis, often in the presence of a photochemically active chemical oxidant, such as persulfate.[11–13] In all such methods an acid hydrolysis step has to be incorporated to convert condensed phosphates to orthophosphate. Goosen and Kloosterboer exploited the combined irradiation and heating properties of a 75 W medium pressure Zn–Cd–Hg lamp to achieve the photolysis and hydrolysis steps.[14] Organic and condensed phosphate species can be distinguished by the failure of the latter to release orthophosphate on photo-oxidation.[15]

This paper demonstrates the use of a novel microwave excited ultraviolet lamp for the rapid photo-decomposition of organophosphate compounds.

## Experimental

The aim of these experiments was to evaluate the performance of a new microwave-excited electrodeless ultraviolet lamp in breaking down a number of phosphate compounds into orthophosphate. Aqueous phosphate solutions were irradiated using the microwave excited lamp and then analysed colorimetrically.

### Standardisation of tetrasodium pyrophosphate decahydrate

Tetrasodium pyrophosphate decahydrate was standardised by titration with 1 mol $L^{-1}$ hydrochloric acid to pH 3.8 using Bromophenol Blue indicator.[16]

### Colorimetric phosphate determination

Phosphate measurement was carried out using an approach adapted from the method described by Murphy and Riley.[17] This procedure, also described by Parsons *et al.*,[18] is based upon the reaction between the sample and a composite reagent containing molybdate, ascorbic acid and trivalent antimony. The resulting complex is reduced to give a blue solution, the absorbance of which can be measured at 885 nm.

The glassware was cleaned with *ca*. 3% (v/v) hydrochloric acid solution, followed by thorough rinsing four times with deionised water. The blue phosphomolybdic complex sticks as a thin film if left in glassware, but can be removed by this washing procedure.

A calibration was achieved using solutions obtained by diluting a $6.01 \times 10^{-3}$ mol $L^{-1}$ anhydrous potassium dihydrogen phosphate ($KH_2PO_4$, analytical grade, BDH) stock solution. Calibration was linear from $1.2 \times 10^{-6}$ mol $L^{-1}$ to $24.0 \times 10^{-6}$ mol $L^{-1}$

### Irradiation experiments

**The microwave excited photolysis lamp.** Constructed in the shape of a beaker, the electrodeless ultraviolet lamp employed in this work is excited by the radiation in a conventional microwave oven. Its emission characteristics are similar to those of a low pressure mercury discharge lamp, giving *ca*. 30% efficiency at 254 nm (*cf*. the *ca*. 6% efficiency at this wavelength of a medium pressure mercury arc lamp). A prototype JenAct UV beaker (JenAct Ltd, Whitchurch, Hants, UK) was used in this research and their technology is licenced to Neutra-plasma Ltd. The walls of the lamp attenuate the microwave energy reaching the samples which, for this work, were held in fused silica tubes mounted in a carousel within the lamp (Fig. 1). A conventional domestic microwave oven (1 kW), modified to give variable continuous (*i.e*. not slowly pulsed) power output was employed for the study. Such modification is not normally necessary for these lamps when moderate power domestic microwave ovens are used on their full power settings. The addition of a microwave sink into the cavity was not necessary for the short irradiation times employed.

**Irradiation procedure.** 2.5 mL aliquots of aqueous phosphate solutions in fused silica tubes (concentrations ranging from $1.84 \times 10^{-5}$ mol $L^{-1}$ to $5.79 \times 10^{-5}$ mol $L^{-1}$) were irradiated for 2 min at full microwave power (900 W energy consumption). When the open beaker system was employed irradiation times of *ca*. 3 min and above gave rise to significant heating of the samples that could cause losses due to boiling. After irradiation the solutions were allowed to cool, transferred to 25 mL volumetric flasks and made up to volume with deionised water, so that the final phosphate concentration was within the calibration range.

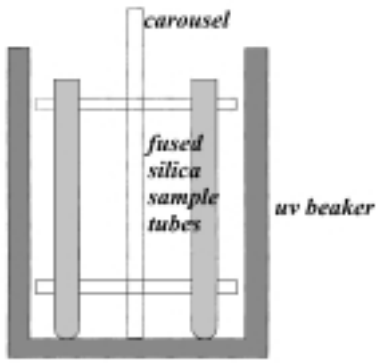


**Fig. 1** Photolysis apparatus.

1 mL of mixed reagent was added to a 10 mL sample, allowed to react for 5 min and then the absorbance of the mixture was measured against deionised water at 885 nm. The blank was checked by carrying out a phosphate determination of the solution prior to its photolysis.

## Results and discussion

### Photolysis and hydrolysis of polyphosphates

Although the polyphosphate would not be expected to be photolysed, the aim of these experiments was to assess the breakdown of the polyphosphate into orthophosphate by effects such as heating by the UV lamp.

2.5 mL aliquots of a $2.78 \times 10^{-5}$ mol $L^{-1}$ $Na_4P_2O_7$ solution were photolysed for 2 min, allowed to cool, transferred to 25 mL volumetric flasks and made up to volume with deionised water. After a 2 min photolysis treatment in the microwave, the average yield was (1.0 ± 0.5)% (1.0% with a standard deviation of 0.5). This reflects the fact that polyphosphates cannot be measured by the Phosphomolybdenum Blue method and that a small orthophosphate impurity was either present in the original pyrophosphate or was generated by the microwave treatment.

The conversion of polyphosphates to orthophosphate by a conventional acid hydrolysis step was tested by using pentasodium tripolyphosphate. 125 μL of sulfuric acid (7 + 45) solution was added to each 2.5 mL sample aliquot. Samples were then heated in a water bath (95 °C) for 2 h. After cooling and dilution to 50 mL with deionised water the samples were analysed for orthophosphate. A yield of (100 ± 2)% was obtained.

Attempts to carry out this acid hydrolysis by microwave heating were unsuccessful. Overheating of the samples occurred within *ca*. 1 min resulting in sample losses due to bumping of between 8 and 45% and yields of 31 to 70% within the same batch.

### Breakdown of organophosphate compounds

In these experiments two organo-monophosphate compounds [β-glycerophosphate disodium salt, 4-nitrophenylphosphate bis(cyclohexylamine) salt] and one organo-polyphosphate compound (adenosine 5′-triphosphate disodium salt) have been studied.

**β-Glycerophosphate.** A $1.0 \times 10^{-4}$ mol $L^{-1}$ solution of the disodium salt of β-glycerophosphate (Sigma, Poole, UK) was photolysed in 2.5 mL aliquots and then analysed for phosphate. Following a 40 s irradiation at full microwave power, an orthophosphate yield of (87.2 ± 1.3)% was achieved that increased to (95.7 ± 2.2)% with 2 min irradiation. With a 2 min 50 s photolysis the yield increased to (98.4 ± 0.9)%.

**4-Nitrophenylphosphate bis(cyclohexylamine) salt.** A $1.0 \times 10^{-4}$ mol $L^{-1}$ solution was photolysed in 2.5 mL aliquots for 2 min 50 s giving an average orthophosphate yield of (94.8 ± 3.1)% .

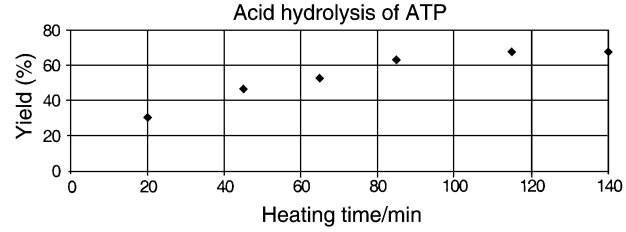


**Fig. 2** Yield *vs*. heating time in water bath (95 °C) for the acid hydrolysis of an ATP solution

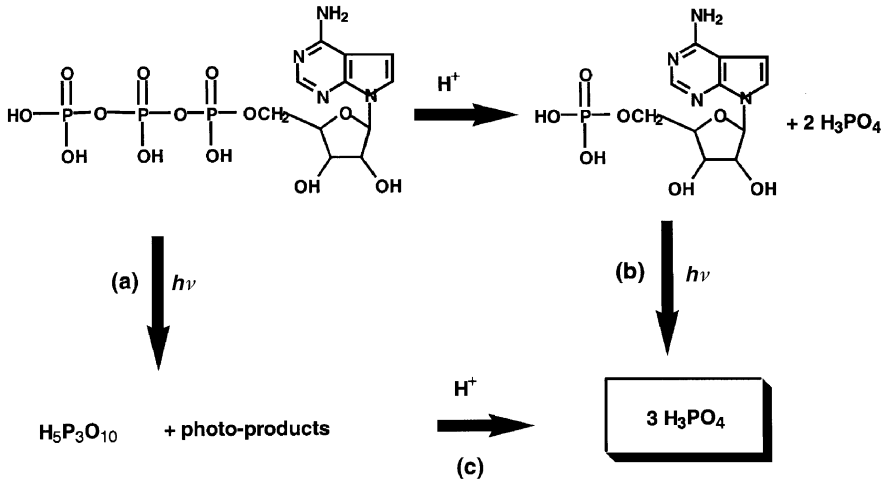


**Fig. 3** Photo-decomposition and acid hydrolysis of ATP

**Adenosine 5′-triphosphate (ATP).** Acid hydrolysis of ATP resulted in the release of two phosphate units from the ATP molecule (Fig. 2). The third P-atom remained attached to the adenosine group (Fig. 3).

The photolysis of a $1.84 \times 10^{-5}$ mol $L^{-1}$ ATP (Sigma, 99–100%) solution resulted in an average orthophosphate yield of 9 ± 1%. Either the photolysis does not release significant quantities of orthophosphate or it breaks the bond between the adenosine and the triphosphate group (Fig. 3) and hence no phosphate can be measured since the method is not sensitive to the triphosphate that is released.

The combination of an initial photolysis of ATP followed by acid hydrolysis resulted in an average yield of (104 ± 2)%, indicating the complete conversion of ATP into orthophosphate. The acid hydrolysis, however, cannot at present be achieved in the microwave due to overheating problems.

It is not possible from this work to distinguish between the possible mechanisms of photo-decomposition that can occur during irradiation. Whilst with some compounds decomposition may occur by direct excitation of the analyte molecule, it is to be expected that much of the decomposition will have resulted from the photochemical generation of hydroxyl and oxygen radicals generated from dissolved oxygen in the samples. The free radical population could be enhanced by the addition of photochemically active agents such as hydrogen peroxide or sodium persulfate, but at the expense of added complexity due to the need to destroy residual reagent after irradiation and with increased potential contamination from reagent impurities.

## Conclusions

The microwave-excited UV lamp has proven to be a very effective means of breaking down organophosphate compounds. Complete recoveries of orthophosphate from the disodium salt of β-glycerophosphate and 4-nitrophenylphosphate bis(cyclohexylamine) salt have been achieved in a 2–3 min photo-decomposition period. The method is simple, rapid, and does not require the addition of any oxidising agent. The photolysis of adenosine 5′-triphosphate was consistent with the photo-decompostion being limited to the organic moiety releasing triphosphate. Subsequent hydrolysis of the released polyphosphate species could be readily carried out by acid hydrolysis. It has not, however, as yet proven possible to employ the microwave oven to carry out this breakdown due to overheating and sample loss.

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