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The importance of chain length for the polyphosphate enhancement of acidic potassium permanganate chemiluminescence☆

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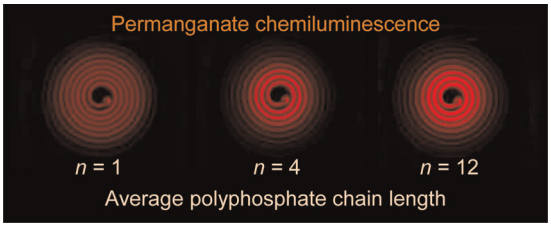
HIGHLIGHTS

- Polyphosphates characterised by titration, NMR and ion chromatography.
- Different enhancement of permanganate chemiluminescence.
- There is a minimum polyphosphate chain length required for a large enhancement.
- No further advantage with much longer chain lengths.
- Optimum concentration of polyphosphate is dependent on the analyte.

GRAPHICAL ABSTRACT



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ABSTRACT

Sodium polyphosphate is commonly used to enhance chemiluminescence reactions with acidic potassium permanganate through a dual enhancement mechanism, but commercially available polyphosphates vary greatly in composition. We have examined the influence of polyphosphate composition and concentration on both the dual enhancement mechanism of chemiluminescence intensity and the stability of the reagent under analytically useful conditions. The average chain length (n) provides a convenient characterisation, but materials with similar values can exhibit markedly different distributions of phosphate oligomers. There is a minimum polyphosphate chain length (~6) required for a large enhancement of the emission intensity, but no further advantage was obtained using polyphosphate materials with much longer average chain lengths. Providing there is a sufficient average chain length, the optimum concentration of polyphosphate is dependent on the analyte and in some cases, may be lower than the quantities previously used in routine detection. However, the concentration of polyphosphate should not be lowered in permanganate reagents that have been partially reduced to form high concentrations of the key manganese(III) co-reactant, as this intermediate needs to be stabilised to prevent formation of insoluble manganese(IV).

1. Introduction

Acidic potassium permanganate was first used for chemiluminescence detection in 1975 [1] and has subsequently been utilised for an extensive range of analytical applications in pharmaceutical, clinical, forensic, food and agricultural settings [2,3]. The

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characteristic red emission of light from redox reactions with permanganate originates from an electronically excited Mn(II) species, thought to be generated by reduction of the immediate Mn(III) precursor by the radical oxidation intermediates of the analyte [4–6]. Several different compounds have been found to enhance the chemiluminescence, such as low molecular weight aldehydes, sodium thiosulfate and sodium polyphosphates, but their mechanisms are not yet fully understood [2,3].

Polyphosphates (chains of four or more repeating phosphate units) are a popular choice of enhancer due to their innocuous nature and reported 50-fold increases in permanganate chemiluminescence intensity [2,3]. Although the mechanism of enhancement is yet to be completely elucidated, their presence in the reaction mixture induces a shift in the maximum emission wavelength from approximately 734 nm to 689 nm, indicating a strong interaction with the emitting species [6]. A dual mechanism of enhancement has been postulated [6], which includes stabilisation of the Mn(III) precursor with respect to Mn(IV) oxides that would otherwise flocculate under the mildly acidic conditions [7–10], and formation of protective "cage-like" structures around the Mn(II) emitter that inhibit nonradiative relaxation [6]. The shorter chain ortho- and pyro-phosphates also prevent disproportionation of Mn(III), but they are not believed to form protecting structures around the emitter, as they do not enhance the emission to the same extent as polyphosphates, and there is no blue shift in the emission spectrum [6].

Commercially available sodium polyphosphates, including 'sodium hexametaphosphate' or Graham's salt [11], are in fact a complex mixture of mostly linear oligomers with a wide range of chain lengths [12]. These products can be characterised by their average number of phosphate atoms per oligomer, or average chain length (n), typically ranging from 4.5 to 18 [11]. Linear polyphosphates generally exhibit stronger complexing power relative to their cyclic counterparts, arising from the greater net charge at each end of the chain compared to the middle groups [11]. Manganese polyphosphate complexes tend to be more stable as the chain length increases, but in this case the end groups have a lesser influence on complexing power because their contribution to the overall charge of the molecule is reduced [13]. Polyphosphates from a variety of sources have been used to enhance chemiluminescence reactions with permanganate [3], but the influence of the average chain length on emission intensity is not known. It is also unknown why the greatest enhancement requires that the polyphosphates be present in large excess (e.g. 1% m/v) compared to permanganate (1.0 mM) [3,14], though it has been postulated that these conditions favour the formation of the protective cage-like structures and help maintain their structural integrity throughout the reaction [6]. It is also possible that such large excesses are required to ensure sufficient quantities of the oligomers of specific lengths.

Herein, we explore a series of commercially available polyphosphate materials as enhancers of permanganate chemiluminescence, examining the influence of polyphosphate structure and concentration on both the enhancement of chemiluminescence intensity and the stability of reagent solutions under analytically useful conditions.

2. Experimental

2.1. ^{31}P NMR

Solution ^{31}P NMR was performed by dissolution of polyphosphates (approximately 70 mg) in 0.6 mL deionised water and 0.1 mL deuterium oxide (for signal lock). Phosphorous NMR measurements were recorded on a Bruker AVANCE 500 spectrometer (Bruker, Karlsruhe, Germany) operating at 202 MHz, with an acquisition time of 1.63 s. Temperature was regulated at 25 °C, and 64 scans were collected. Chemical shifts were referenced to H_3PO_4 in acetone. The well-established Eq. (1) was used to calculate the average chain length (n) of each polyphosphate sample [15], where PP1 refers to terminal (end group) phosphates, PP2 and PP3 to second and third position phosphates, and PPn to the inner phosphates:

$$n = \frac{(\mathrm{PP1} + \mathrm{PP2} + \mathrm{PP3} + \mathrm{PP}n) \times 2}{\mathrm{PP1}} \quad (1)$$

2.2. Titration

A modified end-group titration without hydrolysis [16] was performed using a Metrohm 907 Titrando (Metrohm, FL, USA) and controlled by Tiamo 2.3 software. Dilute hydrochloric acid solution (2 M) was prepared from analytical grade concentrated hydrochloric acid (32% w/w, Chem Supply, Gilman, SA, Australia). Sodium hydroxide (0.1 M) was prepared from sodium hydroxide pellets (Ajax Finechem, Taren Point, NSW, Australia) and standardised against analytical reagent grade potassium hydrogen phthalate (Fisher Scientific, Loughborough, Leicester, UK). Polyphosphate samples were prepared by complete dissolution in deionised water (2% m/v). The average chain length was calculated using the procedure detailed by Griffith [16].

2.3. Flow injection analysis (FIA)

The analytes were injected (70 μL) on a simple two-line FIA manifold with an automated six-port valve (Valco Instruments, Houston, TX, USA) into a deionised water carrier stream, which merged at a T-piece with the acidic potassium permanganate reagent prior to entering a coiled-tubing detection flow-cell comprising 0.8 mm i.d. PTFE tubing (DKSH, Caboolture, Queensland, Australia). The carrier and reagent lines were propelled through 0.8 mm i.d. PTFE tubing (DKSH) at 4 mL min^{-1} using a peristaltic pump (Gilson Minipuls 3, John Morris Scientific, Balwyn, Victoria, Australia) with bridged PVC tubing (DKSH). The flow-cell was mounted flush against the window of a photomultiplier tube (Electron Tubes model 9828SB; ETP, NSW, Australia) encased in a light tight housing and powered by a stable power supply at 950 V. Chemiluminescence intensities were documented with a chart recorder (YEW type3066, Yokogawa Hokushin Electric, Tokyo, Japan), and the peak heights were measured manually.

2.4. Ion chromatography

Chromatographic analysis was carried out using an ICS 3000 chromatography system (Dionex, Thermo Scientific, Sunnyvale, CA, USA). The system was equipped with an autosampler, eluent generation system, anion suppressor and electrochemical conductivity detector. Chromeleon software (version 7.1, Dionex) was used for data acquisition and instrument control. Separation was carried out using a 250 × 4.0 mm ID column IonPac AS-19 (Dionex), with a 200 μL injection volume and 1 mL min^{-1} flow rate. A 60 min potassium hydroxide gradient was used, starting at 40 mM and increasing linearly to 100 mM over the first 10 min, then held at 100 mM for the remaining 50 min. The column was re-equilibrated for 15 min prior to subsequent analyses. Samples were prepared at 1000 ppm and standards at 200 ppm in a 40 mM potassium hydroxide solution, and analysed in duplicate.

2.5. Spectrophotometric monitoring

A Cary 300 Bio UV–vis spectrophotometer (Varian, Mulgrave, Victoria, Australia) was used to measure the absorption of permanganate solutions in a 10 mm quartz cuvette. Sodium thiosulfate was added to the potassium permanganate solution