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Review

Advances in the use of acidic potassium permanganate as a chemiluminescence reagent: A review

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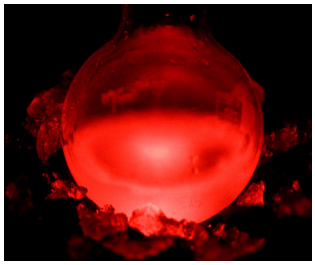
HIGHLIGHTS

- Analytical applications of acidic potassium permanganate chemiluminescence.
- Discussion of emitting species and light-producing reaction pathways.
- Influence of enhancers such as polyphosphates, formaldehyde and sulfite.
- Clinical, forensic, food science, agricultural and environmental applications.

GRAPHICAL ABSTRACT



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ABSTRACT

We review the analytical applications of acidic potassium permanganate chemiluminescence published since our previous comprehensive review in mid-2007 to early 2013. This includes a critical evaluation of evidence for the emitting species, the influence of additives such as polyphosphates, formaldehyde, sulfite, thiosulfate, lanthanide complexes and nanoparticles, the development of a generalized reaction mechanism, and the use of this chemistry in pharmaceutical, clinical, forensic, food science, agricultural and environmental applications.

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Jacqui L. Adcock completed a Bachelor of Forensic Science (Honours) at Deakin University in 2003. Her PhD, received in 2008, included a comprehensive review of permanganate chemiluminescence and a series of experiments that elucidated the key light-producing pathways of permanganate reactions. Jacqui's post-doctoral research has included the development of new applications of fast comprehensive two-dimensional gas chromatography at RMIT University (Australia) and Firmenich (Switzerland), followed by a return to Deakin University as an Australian Research Council Postdoctoral Fellow (Industry) to examine enzymatic synthesis, microencapsulation and biological evaluation of a new class of omega-3 derived functional food ingredients.

Neil W. Barnett received a BAppSc from the Royal Melbourne Institute of Technology in 1978, a PhD from the University of Manchester in 1986 and a DSc from Deakin University in 2005. He is a fellow of both the Royal Society of Chemistry and Royal Australian Chemical Institute and is a member of the Australian Research Council College. As Professor of Analytical Chemistry in the Centre for Chemistry and Biotechnology at Deakin University, Neil leads a group investigating the chemistry and applications of chemiluminescence plus novel multidimensional liquid chromatography. He has published over one hundred and seventy papers in major international journals.

Colin J. Barrow is Chair of Biotechnology and Director of the Centre for Chemistry and Biotechnology at Deakin University. He graduated with a PhD from the University of Canterbury in 1988 and has extensive industry and academic experience. Colin's research is primarily focused on the processing and production of omega-3 lipids, and the use of nano-biotechnology to produce and utilize peptide and protein materials for a variety of industrial and medical purposes. He has approximately 150 peer-reviewed publications, several patents, has presented at numerous conferences, and is a founding member of the International Society for Nutraceuticals and Functional Foods (ISNFF).

Paul S. Francis received a BSc (Hons) in 1999 and a PhD in 2003 from Deakin University. He currently holds an Australian Research Council Future Fellowship, administered by Deakin University, with La Trobe University (Australia) and the University of Manchester (U.K.) as Host Institutions. Through this fellowship, Paul heads a large collaborative programme of research focussed on the development of new highly sensitive luminescence-based detection systems. He has over 100 publications and has been recognized by honours such as a Victoria Young Tall Poppy Science Award (The Australian Institute of Policy and Science), and the Robert Cattrall Medal (Royal Australian Chemical Institute).

1. Introduction

Although the use of potassium permanganate in chemiluminescence reactions in acidic aqueous solution can be traced back to the early twentieth century investigations of Harvey [1] and Grinberg [2], the reagent was not exploited for analysis until Stauff and Jaeschke's determination of sulfur dioxide in 1975 [3]. These and other researchers continued to explore the detection of inorganic species, but the predominant use of acidic potassium permanganate as a chemiluminescence reagent has become the detection of organic compounds, beginning with the determination of morphine by Townshend's group in the mid-1980s [4–7].

In 2001, researchers from our laboratory prepared a review of acidic potassium permanganate as a chemiluminescence reagent, including its historical origins and a chronological account of analytical applications [8]. In 2007 we re-examined this area of research in another comprehensive review [9], with specific foci on reaction conditions, influence of enhancers, relationship between analyte structure and chemiluminescence intensity, and the determination of pharmaceuticals, biomolecules, antioxidants, illicit drugs, pesticides and pollutants. In both reviews, we evaluated the often-conflicting proposals for the nature of the emitting species in light of contemporary evidence [8,9]. Since our last major review of this area, there have been over 170 new publications concerning the use of permanganate as a chemiluminescence reagent, which have expanded the scope of the reagent and provided new insight into the reaction mechanisms and emitting species. We now present a comprehensive account of both the fundamental understanding and analytical applications of acidic potassium permanganate chemiluminescence published from mid-2007 up until early 2013, in journals indexed in the American Chemical Society's Chemical Abstracts (accessed through SciFinder Scholar). This includes a significant number of Chinese language articles, which for completeness we have included in Tables 1–3. In our discussion, however, we have predominantly focussed on papers appearing in English language journals for reasons of correct interpretation of results. We have omitted discussion of chemiluminescent reactions with permanganate in alkaline