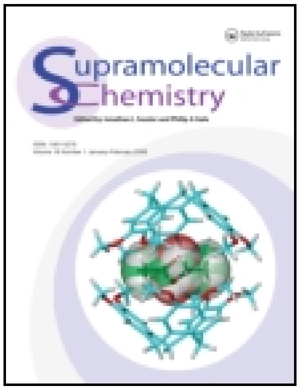

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Colorimetric iodide detection in water: a new photo-activated indicator system

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Colorimetric iodide detection in water: a new photo-activated indicator system

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The photo-induced conversion of iodide to triiodide is an iodide-specific reaction that has now been optimised to produce a reaction-based indicator system for the iodide anion that functions in water. The observed signal (based on the triiodide anions produced upon photo-irradiation) was further amplified with starch (amylase) to produce a signal that can be detected easily by the naked eye. This approach not only allows for the yes/no discrimination of I^- over other anions, it also permits detection of the iodide anion at concentrations of $\geq 30\,\mu M$ by simple visual means, as well as in iodised table salt.

Keywords: iodide indicator; sensor; chemosensor

In recent years, a large number of artificial anion receptors have been synthesised and many have been studied as potential tools for detecting analytes of biological and environmental importance (*1*). In the context of this effort, various hydrogen bonding receptors have been developed and many have found to afford excellent anion selectivity. A subset of these have been further modified to create the so-called chemosensors that can signal the presence of a given anion or class of anions via an easy-to-monitor physical change (redox potential, spectral features, visible colour differences). However, most hydrogen bonding receptors (locks) need be created with a specific shape to fit tightly to their targeted analytes (keys). The creation of these specific structures may require multi-step syntheses to produce a receptor with the required design characteristics. In addition, the efficacy of most common hydrogen bond-based anion receptor motifs diminishes in polar environments. Several approaches have been put forward recently in an effort to overcome this latter constraint (*2*), one of which involves the use of the so-called reaction-based indicators (*3*). Reaction-based indicators, which rely on analyte-specific reactions coupled in some way to a signalling moiety, offer the potential for anion-specific detection without the need for extensive synthesis. So far, this promise remains far from realised. Quite recently, a number of cyanide reaction-based indicators have been reported. This development likely reflects the wide variety of cyanide-specific reactions, such as the cyanohydrin reaction, the benzyl-cyanide rearrangement and related reactions, and various cyanide addition reactions including ligand exchange processes (*4*). In fact, efforts to create modern anion-targeting reaction-based indicator systems that go beyond cyanide are more limited (*3*). For instance, no iodide-specific indicator that functions in water or permits (yes/no) binary selectivity over other anions has been reported to date (*5*). Here, we report such an iodide-specific indicator. It relies on a process of UV photo-excitation to produce the triiodide anion and amylose (water soluble starch) to produce an easy-to-monitor colour change. This new reaction-based indicator protocol affords complete yes/no discrimination of iodide relative to other simple test anions and permits detection of the iodide anion at the ≥ 30 mM level in water by simple visual means. In addition, the potential utility of this protocol is established by demonstrating its use in determining the presence of iodide ions in iodised table salt marketed in the USA. This approach relies completely on off-the-shelf components and does not require any synthetic work. This makes it appealing for use in this and other iodide-sensing applications.

The photo-induced conversion of iodide to triiodide has been studied recently (*5b*). However, it is yet to be utilised to produce a viable iodide anion indicator. Presumably, this reflects the limitations in the nature of the reaction, as discussed subsequently in this paper. However, the basic charge-transfer-to-solvent component of the overall process (which produces iodine radicals) has long been recognised and well studied in the arena of physical chemistry (*6*). These radicals then react with iodide and, after undergoing disproportionation, give rise to the triiodide (I_3^-) and iodide (I^-) anions as shown in Scheme 1 (*7*). Triiodide is a major ingredient in iodine tincture, which is used to disinfect wounds and to sanitise surface water for drinking under field conditions.

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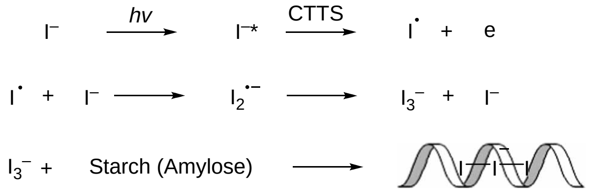

Scheme 1. Chemical transformation thought to underlie the new iodide anion detection protocol described in the text.

The triiodide anion is dark brown, and thus, in principle, can be used as a marker for the presence of iodide anions via the photo-irradiation protocol of Scheme 1. However, the extinction coefficient of the triiodide anion is not high ($\lambda_{\max}$ (ε) = 360 nm ($1.7 \times 10^4\, M^{-1}\, cm^{-1}$ in *t*-BuOH)) (*8*). Therefore, we sought a means of enhancing its colour so as to have a better 'read-out' indicator for the initial iodide anion. With this goal in mind, we reasoned that the addition of amylose (i.e. water-soluble starch) could be used to improve the colorimetric response. Starch is a well-known indicator for molecular iodine, with the actual species detected being the triiodide anion, which is formed *in situ* upon addition of an iodide salt, such as KI, to I_2 in the presence of water. Amylose (starch) wraps around the triiodide anion giving rise to a complex with a dark blue colour (*9*). To the extent that this same highly pigmented complex is produced and the same colour changes (from colourless to a navy blue colour) occur when the triiodide anion is generated directly from iodide via photo-irradiation, the use of starch should allow for the simple colorimetric detection of iodide as per Scheme 1.

To test the validity of the above hypothesis, the photo-induced $I^- \rightarrow I_3^-$ conversion reaction was explored under a variety of conditions. Surprisingly, the reaction proved highly dependent on the solvent. In protic polar solvents, such as MeOH and water, the reaction does not produce detectable quantities of the triiodide anion, as inferred from a lack of colour change (from colourless to yellow, corresponding to I^- and I_3^-, respectively) and the absence of changes in the UV–vis spectrum. In contrast, an immediate colour change was seen when the iodide anion (as the tetrabutylammonium (TBA) salt) was irradiated in CH_2Cl_2 or acetonitrile using a hand-held UV lamp. In accord with what had been reported in the literature (*10*), the photo-induced $I^- \rightarrow I_3^-$ conversion process also proved highly dependent on acidity. For example, when the photo-irradiation reaction was carried out in MeOH containing *p*-TsOH (3.0×10^{-3} M), a colour change consistent with triiodide formation was immediately seen. However, this same acid at the same concentration proved ineffective in water in that no evidence of I_3^- was seen. On the other hand, the use of conc. H_2SO_4 (100 μl per 2 ml of aqueous KI (≥30 μM) allowed the photo-induced conversion to be carried out in acidic water.

With the above predicative experiments complete, various tests of our proposed indicator strategy were carried out in water. In a first set of experiments, the results of which are shown in Figure 1(a), various quantities of an aqueous potassium iodide stock solution (3.0×10^{-3} in water) were added to cuvettes containing 2 ml of an aqueous sulphuric acid solution (1:20 = conc. H_2SO_4: water (v/v)). The resulting samples were then irradiated with a hand-held UV light (256 nm) for 30 min. The samples containing the highest initial concentration of iodide anion (727 μM) changed from clear to pale yellow as a result of this irradiation process. However, the colour change was not so dramatic that the naked eye detection of the initial iodide anion could be considered unambiguous. To our mind, this uncertainty served to underscore the need for a method to amplify the colour response.

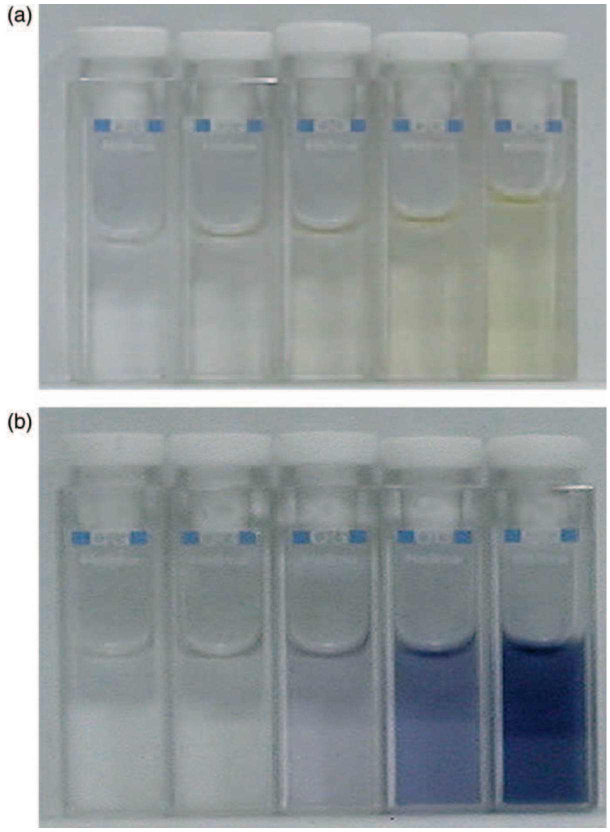

Figure 1. (a) Colour changes observed after the addition of various quantities of KI (stock solution of 3.0×10^{-3} in water) to cuvettes containing 2 ml of an aqueous acidic solution (1:20 = conc. H_2SO_4: water (v/v)) and subjecting to irradiation for 30 min with a hand-held UV lamp. From left to right, the cuvettes contained 0, 115, 222, 414 and 727 μM of the KI stock. (b) Colour changes observed after the addition of various quantities of KI (stock solution of 3.0×10^{-3} in water) to cuvettes containing 2 ml of an aqueous acidic solution (1:20 = conc. H_2SO_4: 0.2% starch in water (v/v)) and subjecting to irradiation for 30 min with a hand-held UV lamp. From left to right, the cuvettes contained: 0, 15, 30, 60 and 115 μM of added KI.

To amplify the triiodide signal, we used soluble starch in accord with the considerations outlined above. To probe the utility of this modification, we conducted the same experiments as before, but in the presence of soluble starch (0.2% in water). In accord with our design expectations, a clean colour change, easily observable by eye, was seen when the initial [KI] $\geq 30\,\mu$M (Figure 1(b)).

In control experiments, we found that the addition of KI to the acidic starch solution (1:20 = conc. H_2SO_4: 0.2% starch in water (v/v)) in the absence of UV irradiation did not lead to a colour change (cf. Figure 2(a)). We thus rule out a colour change arising from side reactions, such as an acid-induced disproportionation of iodide. On this basis, we propose that this new irradiation and starch-based indicator procedure allow for the naked eye-based detection of iodide.

The limit of detection (LoD) under conditions of simple visual detection (initial [KI] $\geq 30\,\mu$M) correlates well with what was seen when the acidic starch solution of Figure 1(b) was treated with a KI_3 standard (cf. Figure S2 of the Supporting Information, available online).

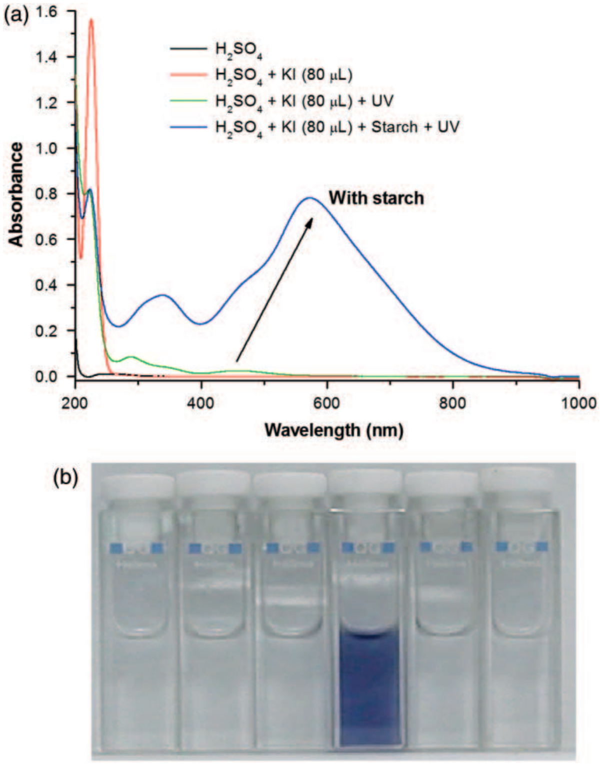

Figure 2. (a) UV–vis spectra recorded after the addition of 80 μl KI (3.0×10^{-3} in water) to a 2 ml aliquot of an aqueous solution (1:20 = conc. H_2SO_4: water (v/v)), followed by UV irradiation for 30 min with or without starch. (b) Colour changes observed after the addition of various anions (80 μl, 3.0×10^{-3} M in MeOH) to 2 ml samples of an aqueous acidic starch solution (1:20 = conc. H_2SO_4:0.2% starch in water (v/v)), followed by irradiation for 10 min with a hand-held UV lamp. From left to right: F^-, Cl^-, Br^-, I^-, HSO_4^- and $H_2PO_4^-$. All anions were added in the form of their respective TBA salts.

The effective LoDs could be pushed lower by using a spectrophotometer. However, for such a more sensitive, instrument-based detection strategy to be practical, a calibration curve had to be constructed. This is because the correlation between the [KI] and the absorbance values proved non-linear, especially at [KI] $< 30\,\mu$M. The observed non-linearity may reflect the fact that the underlying photo-induced triiodide conversion reaction is relatively slow when carried at low KI concentrations resulting in non-equilibrium effects (cf. Figure S3 of the Supporting Information, available online).

To evaluate the selectivity of the present indicator system, we added 80 μl aliquots (3.0×10^{-3} M in MeOH) of various potentially competing anions, including F^- (as the trihydrate), Cl^-, Br^-, HSO_4^- and $H_2PO_4^-$, to the acidic start solution used in the above experiments (all anions were studied as the corresponding TBA salts). No change in colour was observed for any of the anions, either before or after irradiation for 30 min with a hand-held UV lamp (cf. Figure 2(b)). This lack of colorimetric signal production stands in marked contrast to what was seen when 80 μl of I^- (3.0×10^{-3} M in MeOH) was used. In this case, the expected dark blue colour was produced.

Direct interference experiments were also conducted under the same conditions (i.e. 1:20 = conc. H_2SO_4: 0.2% starch in water (v/v)) by carrying out the 10-min UV irradiation protocol in the presence of other anions, including F^-, Cl^-, Br^-, HSO_4^- and $H_2PO_4^-$ (as the TBA salts; 40 μl of each anion, 6.0×10^{-3} M in MeOH, added to 2 ml of the initial solution) with or without TBAI (40 μl of this anion, 6.0×10^{-3} M in MeOH). The expected colour change was seen only in the presence of TBAI (cf. Figure S5 of the Supporting Information, available online). Encouraged by the high specificity seen in these interference experiments, we decided to test whether the present indicator system could be used to test for the presence of KI in iodised table salt. Two different iodised salts (from Morton and Safeway) were thus purchased in the USA. According to the packaging specifications, both these table salt samples were stated as containing 60 μg of KI per g of product. Both samples were thus tested according to the protocol noted above and the results compared to the calibration curve shown in Figure S6 of the Supporting Information, available online. On this basis, the KI content was determined to be 62 ± 0.3 μg/g for the iodised salt from Morton and 42 ± 0.4 μg/g for the iodised salt from Safeway (results of three separate measurements). On the other hand, no evidence of iodide was seen in non-iodised salt samples, such as those commonly marketed in Korea. We take these findings to mean that the present indicator system can be used to detect, at least in a qualitative, binary yes/no sense, the presence of iodide in food-grade table salt. More broadly, this ability to detect trace quantities of iodide in the presence of high concentrations of chloride provides support for our suggestion that the present indicator system could be useful for monitoring iodide in the presence of other potentially interfering ions in water.

The photo-induced triiodide conversion reaction was also monitored by UV–vis spectroscopy, as shown in Figure 2(a). In the absence of an added anion, there is no detectable peak in the UV–vis spectrum. Upon addition of 80 μl of KI (3.0×10^{-3} M in water) to the acidic water solution used in the case of the experiments of Figure 1(a), followed by UV irradiation for 10 min, new peaks appeared at 287, 350 and 460 nm, which are ascribed *inter alia* to the I_3^- anion. In addition, when the same experiment was conducted using the starch solution of Figure 1(b) (i.e. 0.2% in conc. H_2SO_4:-water), a dramatic increase in peak intensity was observed at 574 and 342 nm. To identify the peaks at 574 and 342 nm, we prepared separate triiodide solutions (1:1 mixture of KI and iodine, 3.0×10^{-3} M in MeOH). Upon the addition of 30 μM of this KI_3 solution to the 2 ml original acidic starch sample of Figure 1(b), followed by UV irradiation for 30 min, we obtained the UV–vis spectrum that was found to mirror the one obtained from our indicator system as described above (cf. Figure S4 of the Supporting Information, available online). This experiment provides further support for the reasonable supposition that the colour change and associated spectroscopic effects seen in the case of the indicator protocol reflect the presence of the triiodide anion.

On the basis of these findings, we suggest that the present indicator system is exceptionally selective for the iodide anion, at least when applied in aqueous media. In particular, it allows for yes/no discrimination for iodide over other anions of the same shape, such as F^- (as the trihydrate), Cl^-, Br^- and I^-, a feature that is not usual in the case of hydrogen bond-based receptors and sensors (*11*). We ascribe this high selectivity to the known fact that the photolysis of iodine is easier to accomplish than that of other anions (*12*). This specific reaction-based chemistry permits a level of indicator-based precision that is difficult to achieve using other off-the-shelf visual detection methods.

In summary, the presence of iodide can be easily determined in water using the present indicator system without recourse to any instrumentation other than a hand-held UV lamp. A further advantage is that it requires only off-the-shelf reagents. However, because the optical response monitored is due to the triiodide anion, the intensity of the response (signal) is potentially dependent on the I^-, H^+ and starch concentrations, as well as on the photon energy and flux. However, its convenience and the possibility for further signal amplification via the use of spectrophotometers, charge coupled device (CCD) cameras or the like lead us to predict that this method could have an important role to play in the detection of iodide anion in water. In addition, the present relay approach, wherein an analyte-specific process is coupled to a known indicator reaction to produce a naked eye-detectable response, provides another example of what is emerging a new, possibly general, approach to chemosensor development (*3*). Currently, an ongoing search for new sensing protocols based on this paradigm is underway in our laboratories.

General experimental information, UV–vis spectra and pictures in support of the results cited in this paper are available in the Supporting Information, available online.

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