Voltammetric Detection of Iodide after Accumulation by Friedel's Salt

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Abstract

Friedel's salt, a mineral anion exchanger belonging to the family of the layered double hydroxides (LDHs), was synthesized and used as a novel electrode modifier for the accumulation of iodide species and their subsequent voltammetric determination at carbon paste. Beside the preconcentration features of Friedel's salt towards iodide species, its presence at the electrode surface allowed to evidence the oxidation of molecular iodine into iodate (with transient IO^-), contrary to most carbon-based electrodes, as demonstrated by cyclic voltammetry. Preconcentration was achieved at open circuit and iodide was then detected by differential pulse voltammetry in unbuffered chloride medium. The sensing process was further improved by optimization of the carbon paste composition, the detection medium, and the accumulation time. The detection limit was 0.06 µM (3σ), with linear calibration ranges extending from 0.1 to 1 µM, 1 to 10 µM, and 10 to 50 µM, giving a dynamic range of over several orders of magnitude. The effect of anionic interferences was evaluated and the sensor was applied to iodide analysis in synthetic ground- and seawaters.

Keywords: Iodide, Friedel's salt, Cyclic voltammetry, Differential pulse voltammetry

1. Introduction

Iodine species are potentially hazardous products of nuclear fission. [129]I is one of the more mobile because of its long half-life ($t_{1/2} = 1.7 \times 10^7$ years) and propensity to go into solution as an anion that is not retarded by interaction with ordinary silicate rocks and sediments [1]. Because of the biological role of iodine [2], radioactive species of this element are considered as serious contaminants for both human and environment. As far as long-term storage of radioactive waste (i.e., disposal in deep geological sites) is concerned, the need for regular monitoring of surrounding waters will arise, especially for iodide which is thought to be the major species in anoxic medium. In addition, it was suggested that iodine might be responsible for taste and odor problems in drinking water [3], requiring again its determination in aqueous samples.

Numerous analytical methods have appeared in the literature for the determination of different iodine species in aqueous solutions. For iodide species, titrimetric and spectrophotometric methods [4] were proposed for samples containing high concentrations of the element, while the detection of trace amounts required more expensive and rather complicated instrumental techniques [5–9], such as gas or ion chromatography, inductively coupled plasma atomic emission spectroscopy or mass spectrometry, neutron activation analysis. Most of these methods either required extensive sample pretreatment or involved chemical transformation of iodide before detection to improve the sensitivity. Some electrochemical procedures have been also worked out for iodide sensing. They include normal pulse polarography [10] or cathodic stripping voltammetry [11] at mercury electrode, anodic or adsorptive stripping voltammetry after either potentiostatic accumulation [12, 13], preconcentration at open-circuit and subsequent voltammetric detection at chemically modified electrodes, via the formation of ion pairs [14, 15] or the use of complexing ligands [16] and ion exchange resins [17]. An electrode-supported bilayer lipid membrane containing buckminsterfullerene was also investigated [18]. The main drawbacks of these techniques are either that they require derivatization reactions, or the need for potentiostatic accumulation before detection, or the restricted linear ranges, or even that their sensitivity is too low.

During the last 15 years, electrodes modified with inorganic solids as clays, zeolites, or silica were extensively studied [19–28]. They have reached a level of maturity and understanding which has allowed their implication in electroanalytical chemistry, especially for zeolite- and silica-modified electrodes [24, 26–28]. Analytical applications of clay-modified electrodes are not widespread and limited to cation exchanging materials such as montmorillonite or nontronite. Some recent examples include the analysis of heavy metals [29, 30], pesticides [31], or biologically important compounds [32–35]. The use of anion exchanging clays (hydrotalcite-like clays) in the modification of electrode surfaces was also reported [36–44]. Therias and Mousty [36] reviewed the works carried out before 1995 and more recent examples are available [37–43]. Most of these investigations were, however, devoted to the characterization of the electrochemical activity of the anionic clay itself or to that of anions intercalated within the layered double hydroxide structure. To our best knowledge, electrodes modified with synthetic anionic clays have not yet been exploited for analytical purpose, despite the anion-exchange ability and retention capability of these electrodes were recently evoked [41].

Friedel's salt has been reported as a "poorly understood phase in the CaO-Al_2O_3-$CaCl_2$-H_2O system" [44]. This compound is formed in cements rich in tri-calcium aluminate [45, 46], as in Portland cement which is known as a phase used world-wide for disposal of radioactive, hazardous and mixed wastes [47]. Friedel's salt displays a hydrotalcite-like layered positively charged structure containing charge-compensating anions and water in the interlayer spaces [46]. It belongs to the layered double hydroxide family and would therefore be capable of accumulating anions by ion exchange [48]. Although iodide

sorption of some hydrotalcites has been recently reported [49], the binding ability of Friedel's salt for this species has not yet been investigated. In addition, Friedel's salt has not yet been used as an electrode modifier.

The present investigation involves the synthesis of Friedel's salt, $Ca_4Al_2(OH)_{12}Cl_2 \cdot 4H_2O$, and its use as a novel electrode modifier for sensing iodide. After having demonstrated its ability to exchange Cl^- for I^- species, this properties was exploited by using a carbon paste modified with Friedel's salt for the voltammetric determination of I^- species after their accumulation at the electrode surface. Cyclic voltammetry is first applied to characterize the electrochemical behavior of I^- at such modified electrode. Then, the determination of I^- species is achieved in a two-step procedure (preconcentration and detection) by combining their accumulation at open-circuit by Friedel's salt to their sensitive detection on carbon by differential pulse voltammetry. The optimal experimental conditions are thoroughly investigated, the effect of possible interferent species is discussed, and the method is evaluated for the analysis of iodide in synthetic ground- and seawaters.

2. Experimental

2.1. Chemicals and Reagents

Friedel's salt $Ca_4Al_2(OH)_{12}Cl_2 \cdot 4H_2O$ is synthesized from starting powder $Ca(OH)_2$, $Al(OH)_3$ and $CaCl_2 \cdot 6H_2O$ [Prolabo products] in the molar ratio 3/2/1. Water is added to reach a solid/water ratio equal to 0.5. Stirring is maintained during the synthesis period of about one month, in a glove box under N_2 atmosphere, to avoid monocarbonate contamination. The whole synthesis is made at room temperature. The solid obtained is then dried at room temperature before being recovered as a powdered form for subsequent studies. The iodide form (I-form) of the Friedel's salt is obtained by ion exchange at room temperature from the chloride one (Cl-form), by allowing 2 g of the Cl-form to react with 100 mL of KI (2M) during 3 days under constant magnetic stirring. Both Cl- and I-forms of Friedel's salt are characterized by XRPD using INEL CPS 120 diffractometer with cobalt radiation ($\lambda_{K\alpha} = 17\,903$ Å). Identification of the phases were made using the DIFFRAC-AT program [50] including the ICDD Powder Diffraction Data Base. ASTM file No. 19-0202 and 42-1474 were used to identify Cl- and I-forms of the Friedel's salt, respectively.

All other chemicals were analytical grade reagents and used without further purification. Iodide solutions were prepared from a certified standard of KI purchased from Merck. All solutions were prepared with high purity water (18 MΩ cm^{-1}) obtained from a Millipore Milli-Q water purification system. Adjustment of pH was made by addition of either HCl or NaOH, or by using acetate, phosphate, or ammonium buffers (0.05 M). High purity Ultra F carbon graphite ($<$ 325 mesh) was purchased from Johnson Matthey and mineral oil (Nujol) was obtained from Aldrich. Artificial sea- and groundwaters were prepared according to a reported procedure [51]. Synthetic seawater was made by dissolution of 2.35 g NaCl, 0.50 g MgCl$_2$, 0.39 g Na$_2$SO$_4$, 0.11 g CaCl$_2$, 0.07 g KCl, 0.02 g NaHCO$_3$, and 0.01 g KBr in 100-mL double distilled water. Synthetic groundwater contained 1.83 mM Na$^+$, 0.94 mM Ca^{2+}, 0.31 mM Mg^{2+}, 0.13 mM K$^+$, 2.62 mM Cl$^-$, 1.64 mM HCO$_3^-$, 0.08 mM SO$_4^{2-}$, and 0.04 mM F$^-$. Certified standard water was obtained from Interchim (Montluçon, France).

2.2. Apparatus and Electrodes

Voltammograms were recorded at room temperature. Working electrodes were homemade Friedel's salt modified carbon paste electrodes (MCPEs), the counter-electrode was a platinum wire and a KCl-saturated Ag/AgCl electrode (Metrohm), mounted on a 3 M KCl bridge, served as reference. Cyclic and differential pulse voltammetry measurements were carried out using the μ-autolab potentiostat and GPES (General Purpose Electrochemistry Software) electrochemical analysis system (Eco Chemie). Unless specified otherwise, cyclic voltammograms were obtained at a scan rate of 50 mV s^{-1}, and differential pulse voltammetry was performed with a 75 mV modulation amplitude, a 0.05 s modulation time, and a 25 mV s^{-1} scan rate. All potentials were referred to the Ag/AgCl electrode.

Modified electrodes were prepared as follow. Samples of Friedel's salt and graphite particles in selected ratios were first hand mixed thoroughly for 15 min. The Nujol organic binder (typically 250 mg) was then added to the homogeneous dispersion (typically 750 mg) and mixed thoroughly until obtaining a uniformly wetted paste. The paste was packed into the end of a homemade PTFE cylindrical tube (a.d. 8 mm, i.d. 6 mm) which formed the body of the sensor. It was equipped with a screwing stainless steel piston, allowing mechanical regeneration of the electrode surface by polishing it on a weighing paper. Unmodified carbon paste, used for comparison purpose, was prepared in the same way without adding Friedel's salt to the mixture.

2.3. Procedures

Cyclic voltammetry was first used to characterize the electrochemical behavior of iodide and iodine species at this new electrode, and differential pulse voltammetry was then applied to the quatitative determination of iodide. A typical experiment involves a two-step procedure: an accumulation at open-circuit followed by the voltammetric detection. The modified electrode was immersed for a given period of time in the accumulation cell containing iodide species at a selected concentration. Preconcentration was achieved under constant stirring. The electrode was then removed from the solution, copiously rinsed with water and transferred into the voltammetric cell containing 50 mL of the electrolyte solution (typically 0.05 M unbuffered NaCl). The differential pulse voltammogram was recorded immediately under quiescent conditions by scanning potentials from 0.0 V to +1.2 V. Interestingly, no regeneration step was required because total leaching of iodide into the solution (and concomitant recovery of ion exchange sites within the Friedel's salt) was achieved during the voltammetric detection.

3. Results and Discussion

3.1. Characterization of Friedel's Salt and Ion Exchange

Crystallographic data and structural representations of Friedel's salt [52] and its iodide equivalent [53] are known for these materials prepared from independent synthetic routes. It was first checked that the I-form of Friedel's salt could be obtained by ion exchange from the Cl-form (Eq. 1). Selected 2-θ range (10° to 80°) of X-ray powder diffraction patterns of these two solids indicate that both products are rather pure and that the anion exchange has been completed.

$$Cl_{clay}^- + I_{sol}^- \rightleftharpoons I_{clay}^- + Cl_{sol}^- \qquad (1)$$
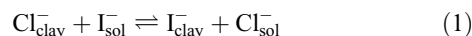
It means that Cl^- anions positioned between the positive sheets $[Ca_2Al(OH)_6]^+$ of the structure have been quantitatively removed and replaced by I^- anions. It is interesting to notice that the I-form of Friedel's salt obtained by ion exchange is the same as that prepared by conventional synthesis from $Ca(OH)_2$, $Al(OH)_3$, and CaI_2.

3.2. Cyclic Voltammetry of Iodide and Iodine Species on Carbon Paste Modified with Friedel's Salt

Preliminary cyclic voltammetry experiments showed very different electrochemical behavior of solution-phase iodide, depending on how they were carried out by using bare carbon paste electrode (CPE) or carbon paste electrode modified with Friedel's salt (noted here as MCPE), and depending on pH (Figure 1). According to previous works [54], iodide (10^{-4} M) can be oxidized on CPE into molecular iodine (Eq. 2), i.e., I_3^- in iodide medium or I_2Cl^- in chloride medium [2], the redox system I_2/I^- being chemically reversible but electrochemically irreversible.

$$I^- - e^- \rightleftharpoons \tfrac{1}{2}I_2 \qquad (2)$$

The slow rate of polarization for the electrogenerated iodine species can be explained by its solubilization into the pasting liquid [12]. This effect was less when increasing the iodide concentration in solution, the I_2/I^- couple becoming quasi-reversible for concentrations higher than 5×10^{-4} M.

The presence of Friedel's salt at the electrode/solution interface changed dramatically the electrochemical response to iodide. In unbuffered solution, the monoelectronic charge transfer

occurring at $+0.59$ V on CPE (Figure 1A) disappeared on MCPE and was replaced by a 6-electron transfer giving an anodic peak at $+1.05$ V (Figure 1B). At the same time, no cathodic counterpart was observed on scan reversal. Note that these curves were recorded directly after immersing the electrode into the solution, so that peak currents are mainly due to solution-phase iodide: in these conditions one can consider that only a negligible part of peak currents is expected to arise from the preconcentration of iodide by Friedel's salt. On both electrodes, the anodic peak currents were linear with the square root of the potential scan rate, indicating that charge transfer processes were limited by diffusion. These results can be rationalized by considering that Friedel's salt induces a local pH higher than 7, preventing the formation of molecular iodine during the oxidation of I^- [55]. Indeed, the dispersion of Friedel's salt powder in water resulted in pH values ranging from 8 to 9 depending on the amount of suspended solids. And, as would be expected, the addition of diluted iodine (< 1 mM) in that suspension resulted in rapid and complete decoloration of the iodine solution because of its disproportionation into I^- and IO_3^- in alkaline medium. For these reasons, the oxidation of I^- at the MCPE in unbuffered solutions involved the direct transformation of I^- into IO_3^- according to a 6-electron transfer reaction (Eq. 3). The absence of transient molecular iodine is further evidenced by the lack of any cathodic signal on scan reversal.

$$I^- + 3H_2O - 6e^- \rightleftharpoons IO_3^- + 6H^+ \qquad (3)$$
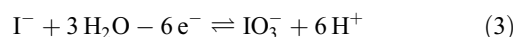
These voltammograms evolved significantly when they were recorded in buffered solutions at pH 4.4, which allowed the existence of molecular iodine. On both electrodes, iodide
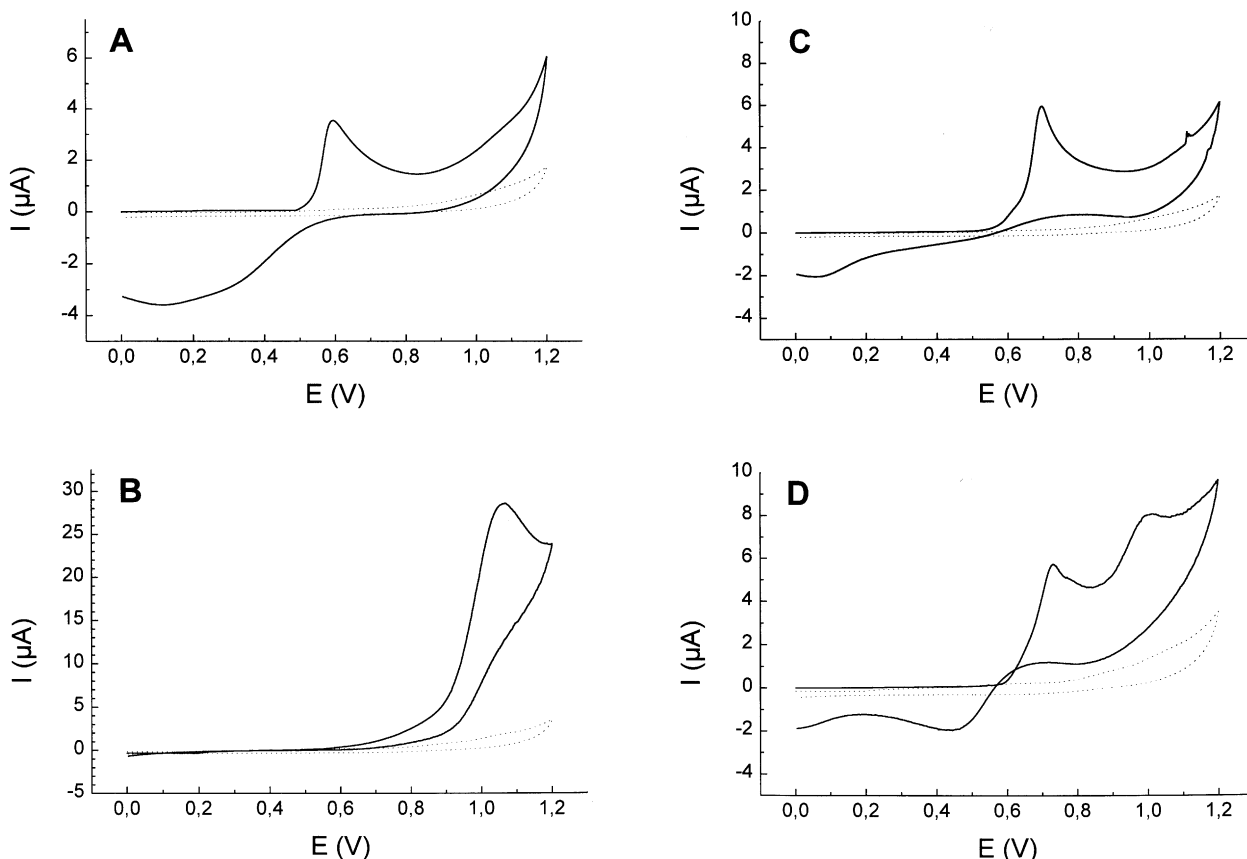

Fig. 1. Cyclic voltammograms recorded in 1.0×10^{-4} M KI by using unmodified (A, C) and Friedel's salt modified (B, D) carbon paste electrodes. Supporting electrolytes were respectively unbuffered 0.05 M NaCl (A, B), and 0.05 M acetate buffer at pH 4.4 (C, D). Scan rate, 50 mV s^{-1}.

underwent a monoelectronic charge transfer at about $+0.70\,V$ corresponding to its oxidation into iodine, but the curve obtained when using the MCPE revealed the presence of some additional peaks: a very small shoulder around $+0.75\,V$, an anodic peak at $1.00\,V$ and a cathodic signal at $+0.45\,V$ on scan reversal. It seems, therefore, that the presence of Friedel's salt at the electrode surface allows the oxidation of electrogenerated molecular iodine (into IO_3^-, most probably via transient IO^-). This is interesting all the more so because iodine did not exhibit any anodic signal at the unmodified carbon paste electrodes made with nonconductive binder, except when using a highly polarizable pasting liquid containing positively charged groups liable to form an ion pair with iodide species [12]. Note that this hypothesis has still to be proven since the anodic peak located close to $+1.00\,V$ could also be due to the oxidation of a part of the iodide directly into iodate. This is otherwise sustained by the fact that the voltammetric behavior of I^- observed in unbuffered $0.05\,M\ NaCl + 0.1\,mM\ HCl$ (pH 4 in the bulk solution) was exactly the same as that observed in the absence of acid (Figure 1B): the diluted strong acid was not sufficient to thwart the basic character of Friedel's salt, allowing therefore the local pH of the electrode/solution interface to be controlled by the mineral modifier.

The distinction between these two possibilities can be definitely stated by studying the electrochemical behavior of molecular iodine in the anodic direction on both CPE and MCPE in buffered solution (i.e., pH 4.4). Results are presented in Figure 2 where it is unambiguously demonstrated that iodine can be oxidized only if carbon paste is modified with Friedel's salt. On CPE, I_2 was not oxidized up to $+1.2\,V$, while it was reduced as expected in a quasireversible monoelectron transfer reaction when scanning potentials towards the cathodic direction (Figure 2A). On MCPE, I_2 was clearly oxidized in an irreversible 5-electron transfer reaction which occurred as a monoelectron prewave located between $+0.55\,V$ and $+0.85\,V$ and a 4-electron wave at about $+1.0\,V$ (Figure 2B). No cathodic counterpart was observed on the reverse scan, indicating the complete consumption (within the diffusion layer) of molecular iodine during the forward anodic scan. It is noteworthy that the resting potential of the electrode in the iodine medium was lower by $250\,mV$ with MCPE than with CPE, arguing again for an anodic activity of I_2 on MCPE. Indeed, when starting the potential scan with MCPE at the resting potential corresponding to that of CPE, significant anodic current was observed before getting the main signal at $+1.0\,V$ (Figure 2B). According to the literature [12], the monoelectron prewave can be attributed to the transformation I_2/IO^- (Eq. 4) and the subsequent 4-electron wave to the IO^-/IO_3^- couple (Eq. 5).

$$\tfrac{1}{2}I_2 + H_2O - e^- \rightleftharpoons IO^- + 2H^+ \qquad (4)$$

$$IO^- + 2H_2O - 4e^- \rightleftharpoons IO_3^- + 4H^+ \qquad (5)$$
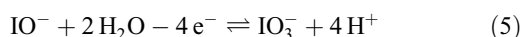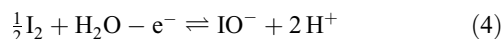
Note that the oxidation of I_2 into IO_3^- is 3–4 times more sensitive than that of I^- into IO_3^- (comparison of Figure 1B with Figure 2B, after normalization of the analyte concentration), which can be explained by lower diffusivity of I_2 compared to I^-. Finally, the driving force allowing the oxidation of I_2 on MCPE, and not on CPE, has to be found in the stabilization of the negatively charged products (IO^- and IO_3^-) by the positively charged structure of Friedel's salt. These anion exchange properties of the modifier will be otherwise exploited hereafter for the
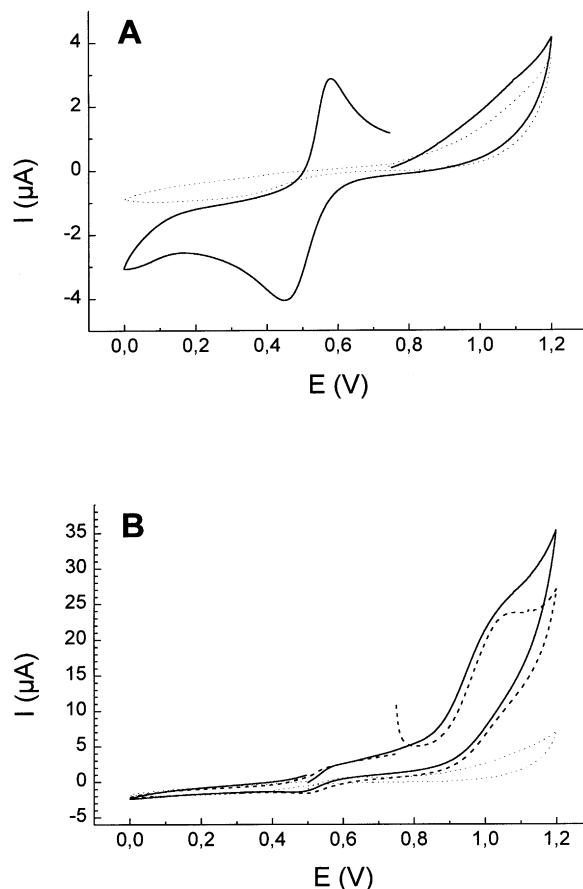
Fig. 2. Cyclic voltammograms recorded in $3.2 \times 10^{-4}\,M\ I_2$ by using unmodified (A) and Friedel's salt modified (B) carbon paste electrodes. Potentials were scanned first from the resting potential ($+0.75\,V$ (A) or $+0.50\,V$ (B)) towards the anodic direction; for comparison purpose, curve (B) was also scanned from $+0.75\,V$ (dotted line). Supporting electrolyte was $0.05\,M\ NaCl + 0.05\,M$ acetate buffer at pH 4.4. Scan rate, $50\,mV\,s^{-1}$.

accumulation of negatively charged I^- species prior to their voltammetric detection.

3.3. Optimization of Detection by Differential Pulse Voltammetry

To demonstrate the ability of the MCPE to preconcentrate I^- species by ion exchange of Cl^-, the initial charge-compensating anion of Friedel's salt, the modified electrode was first immersed in a diluted iodide solution during a selected period of time, then removed and rinsed with water, and finally immersed in a free-iodide electrolyte solution containing chloride ions. The application of a potential scan in the differential pulse mode, performed immediately after immersion of the electrode into the solution, resulted in a well-shaped peak located near $+0.85\,V$ (Figure 3A). This peak is due to the oxidation of I^- species, first accumulated by ion exchange (Eq. 1 shifted to the right) in the analyte cell and then electrochemically detected at the electrode surface after back ion exchange by Cl^- (Eq. 1 shifted to the left) in the detection cell. When using unmodified CPE, no signal was observed because CPE did not exhibit any preconcentration behavior towards iodide. Interestingly, the desorption from the MCPE of the previously accumulated analyte species was fast
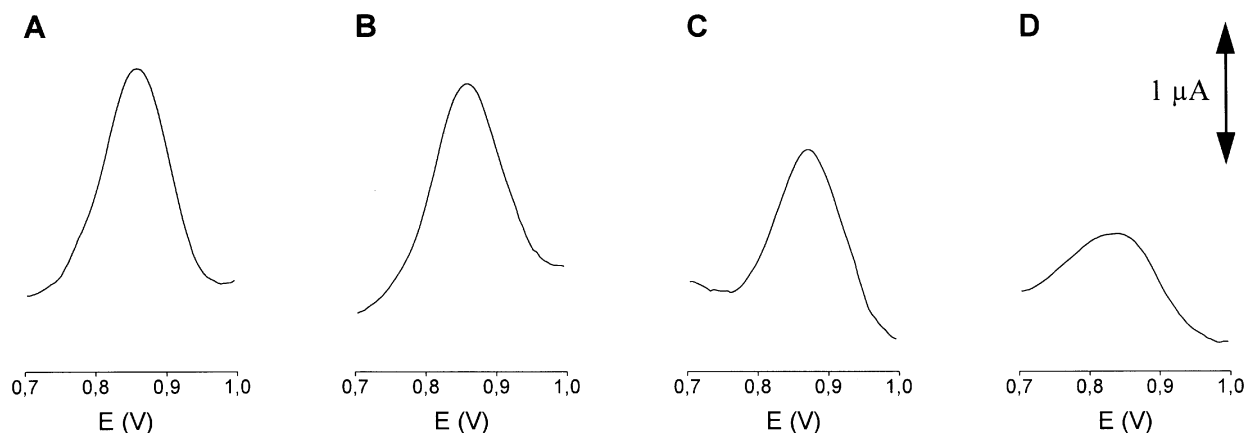
Fig. 3. Differential pulse voltammograms recorded after 2 min accumulation from a 3×10^{-5} M KI solution; detection was achieved in (A) unbuffered 0.05 M NaCl, (B) 0.05 M acetate buffer (pH 4.4), (C) 0.05 M phosphate buffer (pH 7.2), and (D) 0.05 M ammonium buffer (pH 10).

enough to be completed during the time afforded to the voltammetric run, so that a subsequent scan did not reveal any significant signal. No regeneration of the sensor is therefore required as all the ion exchange sites are refilled with chloride during the detection step. Successive analyses (preconcentration and detection) were performed with the same electrode surface and gave a standard deviation of 4% ($n = 5$). The differential pulse voltammetry technique, as well as the oxidation of the analyte to iodate (multiple electron transfer), were chosen to improve the sensitivity of the detection. Several differential pulse parameters were investigated to optimize the detection. Among them, the modulation amplitude was varied between 20 and 200 mV and gave an optimal value of 75 mV. Increasing scan rates resulted in higher peak intensities but contributed to worsen background currents. Overall, the best characteristics in term of signal-to-background current were obtained with a 75 mV modulation amplitude, a 0.05 s modulation time, and a 25 mV s^{-1} scan rate.

The influence of the detection medium composition was then evaluated in order to achieve the most sensitive response. As shown in Figure 3 and Table 1, the effect of pH was rather low since it did not result in more than 50% variation in the voltammetric signals as compared to that obtained without pH control. Anyway, the application of high pHs (with buffers or simply by NaOH addition) lowered the electrode sensitivity, in agreement with the lower oxidation rates for iodide in alkaline medium reported previously [15]. At the opposite, the results obtained at low pHs were less reproducible because of the rather

Table 1. Effect of pH and composition of the detection medium on the voltammetric peak current obtained after 2 min accumulation from 3.0×10^{-5} M KI.

pH (unbuffered) [a]	Peak current (μA)	Composition [b]	Peak current (μA)
2.1	1.2 ± 0.5	NaCl	1.8 ± 0.1
3.2	1.7 ± 0.3	NaBr	0.4 ± 0.2
4.0	1.9 ± 0.2	NaNO$_3$	1.1 ± 0.1
5.5	1.6 ± 0.1	NaClO$_4$	1.3 ± 0.2
6.9	1.5 ± 0.1	Na$_2$SO$_4$	1.2 ± 0.2
7.9	1.4 ± 0.1	Na$_2$CO$_3$	0.2 ± 0.2
10	1.0 ± 0.1		
12	0.9 ± 0.1		

[a] Medium: 0.05 M NaCl; pH adjusted by adding HCl or NaOH in the medium. [b] Concentration: 0.05 M; no pH control.

low stability of Friedel's salt in the presence of proton [46]. Note that the weak effect of pH when it was adjusted by the addition of either a strong acid or a strong base is not very surprising because pH is somewhat levelled locally at the electrode surface by Friedel's salt, as shown above. Moreover, the use of electrolyte anions other than Cl$^-$ resulted always in lower intensities of peak currents (Table 1). This might be due to the fact that Cl$^-$ is the native anion of Friedel's salt and that the insertion of other anions in the layered material can induce unfavorable structure changes. As a consequence, for reasons of sensitivity and reproducibility (recovery of the chloride form of Friedel's salt after detection of iodide), a nonbuffered pH-floating NaCl electrolyte solution will be used throughout as the detection medium.

The composition of the modified carbon paste directly controls the electrode performance, and this condition was optimized by varying both the mineral oil content and the amount of Friedel's salt in the composite matrix. Each of these parameters was examined for the analysis of 5.0×10^{-5} M I$^-$ and was found to affect significantly the voltammetric signals (Figure 4). The results indicate that peak charges reached a maximum when the content of the pasting liquid was around 24 wt.% (Figure 4A). The sharp decrease in the sensor response for higher mineral oil contents is explained by an increase in the electrode surface hydrophobicity, limiting somewhat the accumulation efficiency. Lower contents resulted in less reproducible measurements due to the difficulty of appropriate mechanical smoothing of the electrode surface for a slightly wetted paste. In addition, the voltammetric signals were found to increase linearly as the loading of Friedel's salt was increased up to 30 wt.% (Figure 4B), indicating a preconcentration efficiency directly proportional to the amount of ion exchanger into the paste. Above 30 wt.%, the signals levelled off and even decreased, most probably because the carbon content of the electrode was too low to ensure the complete detection of the accumulated species. In addition, the results obtained with pastes containing more than 25 wt.% Friedel's salt were characterized by rather large dispersion in peak intensities, so that a loading of 20 wt.% was chosen as the most appropriate compromise between high sensitivity and reproducibility, and used throughout for further experiments.

The time allowed for the accumulation of the analyte at open circuit was found to affect the electrode response. This effect is illustrated in Figure 5 for three I$^-$ concentrations, 1.5×10^{-5} M, 2.5×10^{-5} M, and 5.0×10^{-5} M. For short accumulation times, a rapid increase of the voltammetric signals was always observed
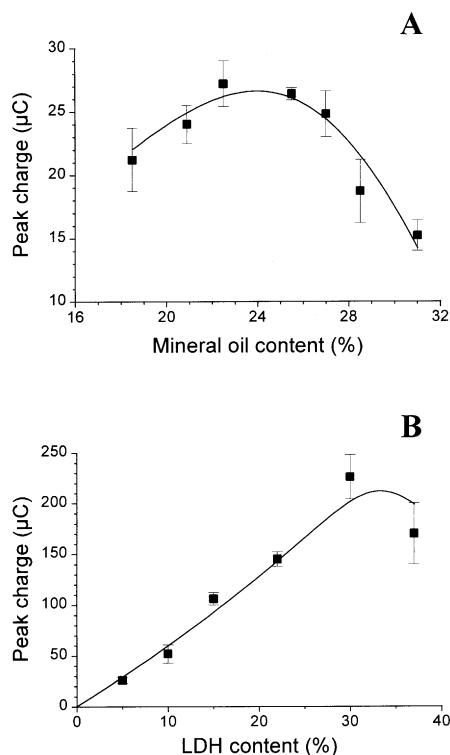
Fig. 4. Influence of (A) the mineral oil content and (B) the Friedel's salt content into the paste on the differential pulse voltammetric response (peak charge) of the modified electrode after accumulation from a 5×10^{-5} M KI solution; (A) 2 min accumulation, and (B) 5 min accumulation. Supporting electrolyte of the detection medium was unbuffered 0.05 M NaCl.
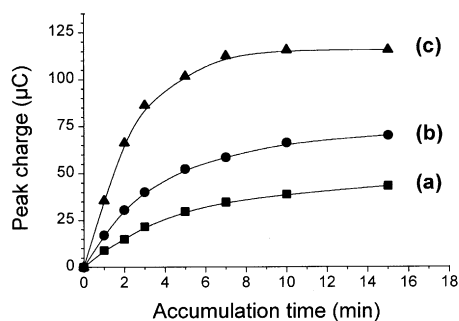

Fig. 5. Dependence the differential pulse voltammetric response (peak charge) of the modified electrode on the accumulation time from a) 1.5×10^{-5} M, b) 2.5×10^{-5} M, and c) 5.0×10^{-5} M KI solutions. Detection medium, unbuffered 0.05 M NaCl; electrode composition, 20% Friedel's salt + 25% oil + 55% graphite.

as the accumulation time increased. They even tended to level off around 5 min for the most concentrated sample while more diluted analyte solutions required longer preconcentration times to get saturation, as illustrated by a slow increase of peak charge between 5 and 15 min accumulation. As a consequence, the increase in the accumulation time in the goal to increase the sensitivity of the detection would be effective only for lower concentrations of iodide.

3.4. Analytical Characterizations

By applying the optimal conditions described above, the voltammetric response of carbon paste modified with Friedel's

salt was examined versus the concentration of I^- over several orders of magnitude. The results are illustrated in Figure 6 where the voltammetric curves are depicted on parts A and B, respectively for the 10^{-7} M to 10^{-6} M and 10^{-6} M to 10^{-4} M concentration ranges, while parts C, D, and E display the corresponding calibration plots constructed from the integration of the crude data. There are several features to notice on this figure. First, the lower analyte concentrations resulted in only one well-defined peak (noted A_3 on the figure) located near $+0.9$ V and corresponding to the direct 6-electron transfer reaction I^-/IO_3^- (Eq. 3). Second, the analysis of higher concentrations showed the progressive emergence of a new peak A_1 around $+0.55$ V and a small shoulder between $+0.65$ V and $+0.70$ V (A_2). According to the above cyclic voltammetry studies, these signals are attributed to the I^-/I_2 and I_2/IO^- redox couples (Eqs. 2 and 4), respectively, while peak A_3 results from both the I^-/IO_3^- and IO^-/IO_3^- redox couples (Eqs. 3 and 5). The apparition of peaks A_1 and A_2 is explained by a progressive decrease in the local pH at the electrode surface, originating from the production of protons during the oxidation of I^-, as more intense as greater was the amount of accumulated iodide species. This was ascertained by recording the same curves in buffered solutions at pH 10 (ensuring the nonexistence of I_2), revealing only the presence of peak A_3, but displaying a significantly lower sensitivity as already stated above. Third, the integration of the voltammetric peaks gave linear calibration plots over the 1.0×10^{-7} M to 1.0×10^{-6} M, 1.0×10^{-6} M to 1.0×10^{-5} M, and 1.0×10^{-5} M to 5.0×10^{-5} M ranges with slopes ($\mu C/\mu M$) and correlation coefficients of 4.6; 0.999, 2.5; 0.998, and 1.4; 0.999, respectively. The detection limit (3σ) was calculated to be 6×10^{-8} M. The lower sensitivity observed for concentrations above 10^{-6} M, and especially above 10^{-5} M, is explained by the lower currents observed for the reaction sequence $I^-/I_2/IO^-/IO_3^-$ compared to the direct oxidation of iodide into iodate.

The influence of various possible interfering anions was evaluated because they can compete with iodide for the ion exchanging sites within the Friedel's salt. The main results are collected in Table 2 where it can be seen that the increase in the interfering anion concentration resulted in a concomitant decrease in the response to iodide, and that this effect was less with monovalent species than with dianions. Nevertheless, a 10 000-fold excess of these anions compared to iodide allowed still the determination of iodide with a decrease in sensitivity of only 5 to 10 times depending on the charge of the interfering anion. Note that high concentrations of thiocyanate caused large currents at potentials above $+0.8$ V preventing proper analysis of iodide in the presence of more than 1 mM SCN^-.

The same calibration experiments as those performed in distilled water were repeated in synthetic ground and seawaters. As would be expected on the basis of interference studies (Table 2), decreases in sensitivity and less attractive detection limits were observed, but the analysis of iodide in these media was still possible in extended linear ranges (between 5×10^{-7} M and 6×10^{-5} M for groundwater, and between 2×10^{-6} M and 1×10^{-4} M for seawater). Overall, the sensitivity in synthetic ground and seawaters was decreased by respectively 2.5 and 6 factors compared to distilled water. Detection limits (3σ) of 3×10^{-7} M and 1×10^{-6} M were achieved in ground- and seawaters, respectively. The proposed procedure was further evaluated for iodide analysis in a certified standard water sample where good accuracy ($99 \pm 3\%$ recovery) was obtained by the standard addition method.
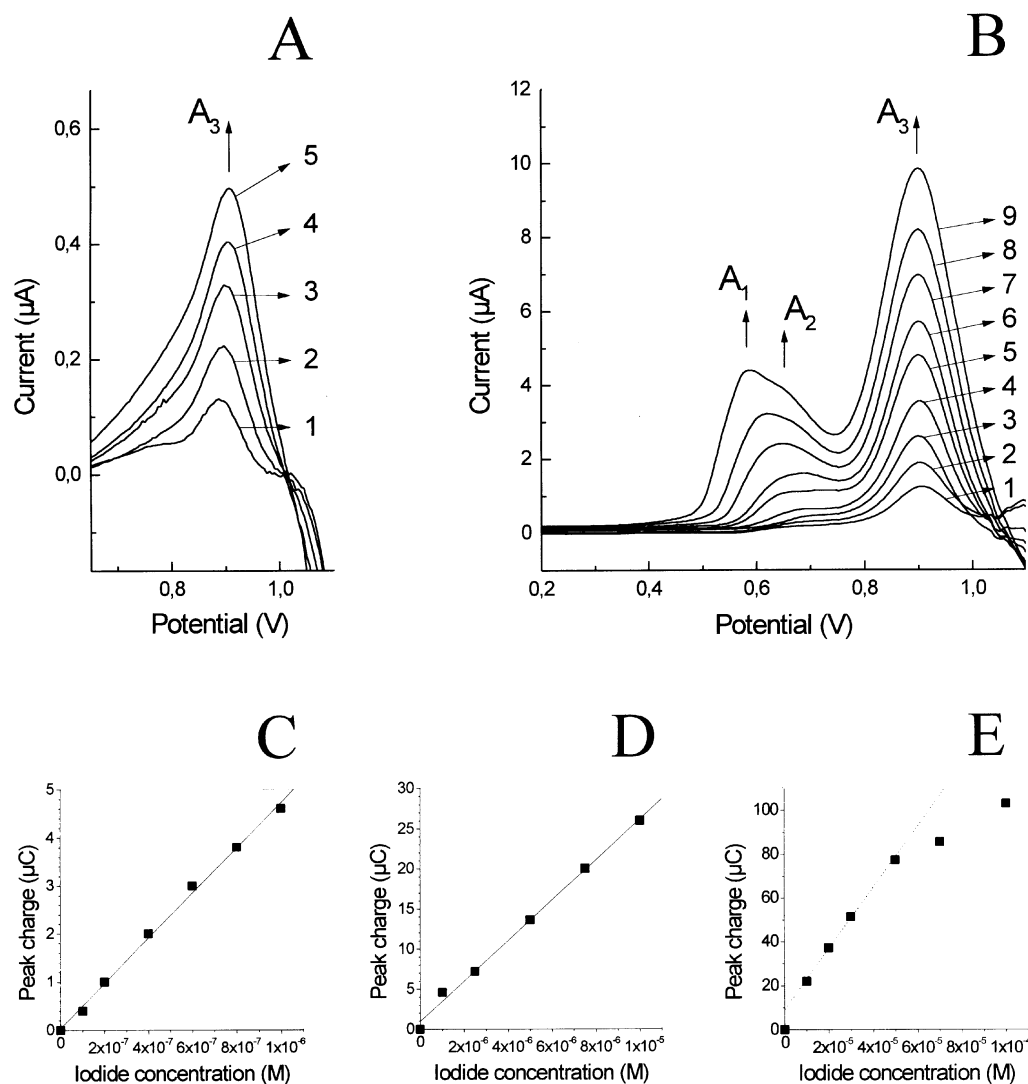
A

B

C

D

E

Fig. 6. Differential pulse voltammograms (background subtracted) obtained for the analysis of iodide in the concentration range between 1×10^{-7} M and 1×10^{-6} M (A), and 1×10^{-6} M and 1×10^{-4} M (B). Accumulation time, 5 min; other conditions as in Figure 5. The corresponding calibration plots obtained from the integration of the voltammetric peaks are also shown for three concentration ranges: 1×10^{-7} M to 1×10^{-6} M (C), 1×10^{-6} M to 1×10^{-5} M (D), 1×10^{-5} M to 1×10^{-4} M (E).

Table 2. Effect of anionic interference on the voltammetric peak area (mC) obtained after 10 min accumulation from a 3.0×10^{-5} M iodide solution containing increasing concentrations of various anions.

Cation concentration	Cl^-	Br^-	NO_3^-	ClO_4^-	SCN^-	CO_3^{2-}	SO_4^{2-}	$C_2O_4^{2-}$
Without added anions	109	112	115	113	108	109	112	109
1.0×10^{-5} M	112	110	110	112	104	110	108	105
3.0×10^{-5} M	108	110	112	107	105	107	96	99
1.0×10^{-4} M	105	104	96	100	95	92	86	75
3.0×10^{-4} M	90	100	85	86	88	65	75	68
1.0×10^{-3} M	73	80	74	72	80	55	48	68
3.0×10^{-3} M	64	55	68	62	115	40	38	65
1.0×10^{-2} M	55	44	54	57	180	32	27	62
3.0×10^{-2} M	50	36	48	54	350	22	23	56
1.0×10^{-1} M	39	28	36	47	–[a]	15	18	35
3.0×10^{-1} M	23	20	21	35	–[a]	11	10	21

[a] not measurable.

4. Conclusions

We have highlighted here the interest of a novel electrode modifier, the Friedel's salt, for the preconcentration of iodide species prior to voltammetric quantification. The presence of this mineral at the electrode/solution interface allowed performing the oxidation of molecular iodine which was normally not possible on conventional carbon paste electrodes. The sensor is sensitive to iodide species and does not require any regeneration step between each measurement because the detection step in unbuffered sodium chloride solution ensures the complete recovery of the initial ion exchange sites. This distinctive feature is the real advantage of Friedel's salt modified carbon paste electrode over the other electrochemical methods while keeping sensitivity and detection limit of the same order of magnitude.

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6. References

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