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Evidence for Photochemical Synthesis of Fluoromethane

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Abstract

Photochemical generation of volatile fluoromethane in a dilute acetic acid medium is demonstrated. Radical halogen atom transfer (XAT) from an intermediate Cu-F transition metal fluorocomplex to abundant $^{\bullet}CH_3$ generated by UV homolysis of acetic acid, rather than direct formation of free $^{\bullet}F$ radicals, is hypothesized as being the synthetic route. The presence of Cu(II) is indispensable for CH_3F formation. GC-MS identification of the gaseous products released from a photolysed 2 % (*v/v*) solution of acetic acid containing 60 mg/L added Cu(II) as a sensitizer confirms synthesis of CH_3F as the volatile fluorinated species, which is not detectable in the absence of Cu(II). Reaction efficiency remains unchanged whether the sample medium is exposed to V-UV radiation (185 nm) or germicidal UV-C radiation (primarily 254 nm and longer wavelengths) from the source. Experimental optimization of generation conditions (pH, irradiation time, UV wavelength, acetic acid concentration, metal ion sensitizer and concentration) was undertaken with a view to elucidation of mechanism as well as maximizing synthetic yield. Although the low yield (<1 %) of CH_3F currently precludes its efficacious use as a means of enhancing analyte introduction efficiency into atomic spectrochemical sources, this study demonstrates successful application of XAT to encompass PVG of the most difficult of the halogens to process in this manner and may provide insights into further studies to ultimately achieve higher yields.

Keywords: fluoromethane generation; photochemical generation; radical halogen atom transfer; transition metal sensitizer.

INTRODUCTION

The importance of the halogens from both essential and toxic perspectives on human health and their determination in environmental and biological samples has been less widely documented compared to the corresponding impacts of metals and metalloids.[1-4] This shortcoming is likely due in large part to a paucity of robust, sensitive and convenient methodology for their quantitation, in particular, for fluorine. The properties of fluorine (high ionization potential and electronegativity coupled with small covalent radius) give rise to problematic issues relating to various detection techniques, especially those based on atomic spectrometry. As the resonance lines of F lie in the vacuum UV, application of conventional atomic absorption methodology is ineffective and molecular absorption spectrometry (MAS), relying on the high temperature formation of stable molecular fluoride species such as GaF[4] and CaF[5], permits detection limits of only 0.16 mg/L to be achieved when coupled with high resolution (HR) continuum source spectrometers. Similarly, application of argon plasmas as sources for emission and mass spectrometry severely underperform compared to other elements due to high excitation (> 10 eV, 95.483 nm, necessitating use of a non-resonance F(I) line at 685.603 nm) and ionization energies (IP = 17 eV) of F. Consequently, there is an insufficient ion population with conventional ICP-MS for detection of F^+ and only HR systems are able to cope with the low mass isobaric interferences in an Ar supported wet plasma, yielding disappointing LODs on the order of 5 mg/L.[6] Older, conventional quadrupole ICP-MS instruments operating in the negative ion mode provided LODs of 0.4 mg/L[7], but these instruments are no longer available.

Similarly to MAS, advantage has recently been taken of sequestering free F as stable polyatomic species having high bond energies and more suitable IPs, such as $[^{138}Ba^{19}F]^+$ (IP = 6.39 eV), improving the LOD to 0.05 mg/L using a modern ICPMS/MS approach[8], prompting an appeal to make available a commercial negative mode ICPMS/MS instrument.[9]

Additional studies have explored the potential of LIBS for detection of F; a detection limit of 20 mg/L was reported by Dudragne et al.[10] based on detection of F(I) emission at 685.604 nm. Foucaud et al.[11] utilized a handheld LIBS system but did not report any estimated LODs when monitoring emission from CaF bands. More recently, Tang et al.[12] reported a LOD of 5 mg/kg for the determination of fluoride in copper ore based on molecular emission from SrF excited in a LIBS plasma.

Although current research activities continue to explore the potential of alternative techniques such as surface enhanced Raman scattering aided by Ag nanoparticles to reach a LOD of 18 µg/L[13] and use of photoelectrochemical detection based on changes in the surface properties of TiO_2 nanorod arrays to permit detection at an unprecedented level of 0.6 ng/L[14], ion chromatography and ion selective electrode methodologies presently remain the workhorses in high throughput laboratories[1,2], yielding limits of detection of 0.1 mg/L[15] and 1 µg/L[16] , respectively.

Apart from direct approaches, it should be noted that amongst derivatization techniques, aqueous fluoride can also be derivatized with triethyloxonium tetrachloroferrate(III)[3] to permit selective matrix separation and sensitive determinations in a wide range of matrices with a LOD of 3.2 µg/L when headspace sampling is coupled with GC-MS. Unfortunately, compared to Cl^-, Br^- and I^-, for which yields of ethylation products are substantial (12, 23 and 54 %, respectively) that for F^- remains at the "trace" level.[17]

Plasma source spectrochemical techniques have greatly benefitted from the improved analyte introduction efficiencies achieved when coupled to analyte vapor generation manifolds[18-20], permitting substantial enhancements in practical limits of detection for some 20 elements.[21]. Apart from traditional hydride generation, photochemical vapor generation (PVG) has been utilized for augmented detection of I[22], Br[23] and Cl[24] with generation yields of 94, 95 and 80 %, respectively. To date, no similar reports exploring application of PVG techniques for fluoride have appeared, although it is clear that significant benefit would accrue from success in such an undertaking.
The focus of this study was to assess the feasibility of synthesis of fluoromethane in dilute acetic acid media utilizing photochemical reactions stimulated by exposure to UV and vacuum UV radiation.

EXPERIMENTAL

Instrumentation. Two photochemical reactors were evaluated. A 19 W thin-film flow-through PVG reactor (Beijing Titan Instrument Co. Ltd., Beijing, China) fitted with synthetic quartz conduits (0.72 mL internal irradiated volume) directly embedded in the low pressure mercury discharge permitted exposure of samples to vacuum UV radiation at 185 nm, as described earlier.[23,24] The second reactor was assembled from a 3 m length of 1.1 mm i.d. PTFE tubing (providing an irradiated volume of 2.0 mL (Alpha Wire Corp, New Jersey) coiled around a low pressure 15 W Hg germicidal lamp (Spectroline, USA), as described earlier.[22] Samples were delivered *via* a Gilson Minipuls 2 peristaltic pump (Mandel Scientific, Villiers, Le Bel, France) at variable flow rates to alter irradiation times but typically at 1 mL/min to yield residence times of the solutions in the UV fields of 43 s and 120 s respectively, for the above reactors.

Effluent from either PVG reactor was directed to a glass thin-film gas liquid separator (GLS) sourced from a model 2600 Tekran Instruments Corporation (Toronto, Canada) mercury analyzer. Waste evacuation from the GLS was accomplished using a separate peristaltic pump. A flow of N_2 passing through the GLS served to strip volatile fluorine species from the liquid phase and direct it *via* a 2 mm i.d. PTFE tube to allow manual sampling with a gas tight syringe for product characterization by GC-MS.

UV-vis spectra of all solutions were acquired on a Cary 5000 UV-vis-NIR spectrometer (Varian Australia Pty Ltd) using a matched set of 1 cm path length quartz cuvettes for reference (blank) and sample compartments. Scans were undertaken from 190 - 700 nm at 200 nm/min.

GC-MS identification of fluorinated products in the gas phase issuing from the GLS was undertaken with an Agilent 6890N gas chromatograph equipped with an Agilent 5975C mass selective detector. Sample injection was performed using a 1 mm I.D. straight liner at 120 °C with a 1:10 split ratio. The separation was obtained within 5.5 min under a 32 °C isotherm on a DB-624 column (6% cyanopropyl-phenyl 94% dimethyl polysiloxane, 60 m length x 0.25 mm I.D. x 1.4 µm film) at a constant 1 mL/min flow of He. The transfer line temperature was 220 °C. The mass spectrometer was operated in electron impact mode (70 eV) using standard settings (ion source temperature 250 °C; quadrupole temperature 150 °C). Full scan mode (*m*/*z* 15-200 Da) was employed for retention time identification of chemically generated CH_3F, whereas Selective Ion Monitoring (SIM, *m*/*z* 15, 33, and 34 Da) was used to monitor the PVG of CH_3F.

Ion chromatographic analyses were performed using a Thermo Scientific system: a Dionex ICS-5000$^+$ Sp-5 sample pump was interfaced to a Dionex AS-AP autosampler. A 25 µL sample volume was injected and elution was performed in isocratic mode (4.5 mM Na_2CO_3, 0.8 mM $NaHCO_3$, 30 min, 30 °C) at 1.0 mL/min flow rate. Ion separation was obtained with a Dionex IonPack AS23 column (4 x 250 mm) connected to an AG23 (4 x 50 mm) guard column. The analytical signal was monitored in suppressed conductivity mode at 35 °C with 25 mA applied to the suppressor (20 Hz sample collection rate).

Reagents and materials. A 25 g/L stock solution of F^- was prepared from NaF (Alfa Aesar, 99 % min); glacial acetic and sulfuric acids were obtained from Anachemia (Montreal), as was aqueous ammonia. Stock solutions (nominally 5000 mg/L as the metal) of various photochemical metal ion "sensitizers" were prepared from $CuSO_4$ (BDH Inc., Toronto), $NiSO_4{\cdot}6H_2O$, $CoSO_4{\cdot}7H_2O$ (Baker Chemical Co., Philadelphia), $Al_2(SO_4)_3{\cdot}14H_2O$ and $CdSO_4{\cdot}H_2O$ (Alfa Aesar). Trimethyloxonium tetrafluoroborate of 95 % purity was sourced from Sigma-Aldrich. Nano-titania photocatalysts included TiNano 40 TiO_2 (Altair technologies, Reno, Nevada) and Degussa Aeroxide TiO_2 P 25 (Evonik Ind., Frankfurt, Germany). High purity (18 MΩ-cm) water was generated in a Milli-Q Advantage system (Millipore Sigma) fed with distilled water and used for preparation of all solutions.

Procedures. Test solutions of 500 mg/L F^- in typically 2 % (*v/v*) acetic acid were employed for all studies. The impact of added metal ion sensitizers at spiked concentrations of 20 - 120 mg/L was studied, both in the absence and presence of 100 mg/L (*m/v*) of either nano TiO_2 or Aerogel P25 photocatalyst. Optimization of PVG conditions using both the 19 W quartz flow-through reactor and the 15 W Teflon-based germicidal reactor was undertaken with respect to irradiation time (by varying the sample solution flow rates in the range 0.5 - 4 mL/min), pH (adjusted to 2, 4, 6 and 10 with either dilute H_2SO_4 or aqueous ammonia) and mass concentration of TiO_2, once the best photosensitizer was identified.

For detection of CH_3F, the GC-MS was first optimized using F^- solutions derivatized with trimethyloxonium tetrafluoroborate[3, 17] whereby retention time and peak assignments for generated fluoromethane were validated by comparison with a NIST library spectrum for CH_3F. Confirmation of fluoromethane arising from PVG and its relative concentration were evaluated by SIM based on relative intensities of the most abundant fluorine-containing ions, i.e., CH_2F^+ and CH_3F^+ at *m/z* = 33 and 34 Da, respectively (mirroring the standard EI mass spectrum of CH_3F

available from the NIST library[25]) arising from the single analyte peak extracted at 5.22 min retention time, separated from the peak of N_2. This permitted the impact of experimental variables on generation of CH_3F to be rapidly assessed.

Based on earlier experience with PVG of Br[23] and Cl[24], a 2 % solution of acetic acid served as the generation medium, although a range of concentrations (0.5, 1, 2, 4 and 6 % *v/v*) was examined for comprehensiveness. Nominal 60 mg/L concentrations of added metal ion sensitizers were studied as this was typical of earlier reported conditions for their impact on the PVG efficiencies of other elements. Irradiation times with the quartz flow-through reactor were varied from 11 - 108 s (flow rates of 0.4 - 4 mL/min), whereas that with the germicidal lamp reactor was maintained at 120 s (1 mL/min flow rate). The transfer gas used with the gas-liquid separator was N_2 at a flow rate of 140 mL/min. All solutions were prepared gravimetrically by spiking appropriate masses of stock solutions / reagents into Milli-Q water. All test solutions were either reagent blanks or contained 500 mg/L F^-. Photolysed solutions containing nano-titania were centrifuged for 10 min at 5000 rpm in a Sorvall Legend X1R centrifuge (Thermo Scientific) prior to IC analysis or acquisition of their UV/vis spectra.

A 500 µL volume of the effluent gas from the GLS was manually taken with a gas-tight syringe and injected into the GC-MS for analysis. Care was taken to collect representative samples of all irradiated solutions evacuated from the GLS such that ion chromatography could be applied to determine changes in the concentration of F^- relative to the non-irradiated solutions. Samples were diluted 25-fold with Milli-Q water and 25 µL volumes were delivered to the IC system *via* an autosampler. Triplicate runs were averaged for all samples and integrated response from F^- was normalized to the detected peak of CH_3COO^- to enhance precision of determination.
UV/vis spectra were acquired on all sample solutions at stages during their preparation and following their irradiation in an effort to detect changes induced by complexation and photolysis.

Safety Precautions. Although fluoromethane is non-toxic, the full suite of volatile product(s) generated in the PVG system (especially in the presence of added metal ion sensitizers) has not been identified and should be considered toxic; adequate ventilation/exhaust and PPE should be used.

RESULTS AND DISCUSSION

Vapor generation enhances sample introduction efficiency for atomic spectroscopy and PVG has earlier proved very successful for synthesis of volatile methyl analogues of I^-, Br^- and Cl^- used for this purpose. Fluoride remains an elusive halide candidate and was examined in this study for generation of stable fluoromethane. Obstacles to successful PVG of F have been highlighted by Leonari and Sturgeon;[21] direct generation of $^{\bullet}F$ radicals requires vacuum UV photons of higher energy than available from low pressure mercury discharge lamps.[21]. Similar difficulties were noted with Cl[24], but less so with Br[23], which possesses an absorption transition lying on the cusp of available high energy photons from the discharge, i.e., 177.6 nm. Most recently, use of metal ion "sensitizers" has proven indispensable in augmenting PVG yields for a number of elements which could not otherwise be usefully coupled to spectroscopic detection techniques to enhance analytical performance. Thus, Cd^{2+} and Fe^{3+} augmented PVG of As;[26,27] Cd^{2+} enhanced generation of W[28] and reaction of Se(VI);[29] $Co^{2+}$and Ni^{2+} augmented Pb;[30] Cu^{2+} was effective for Cl[24] as well as Ir and Rh;[31] Fe(III)[32], and a mixture of Co^{2+} and Cu^{2+} were beneficial for Mo;[33] Fe^{3+} enhanced Bi generation;[34,35] Fe^{2+} improved efficiency for Te[36] and Co^{2+} significantly enhanced PVG of Tl.[37] Currently, their mechanism(s) of action remain rather speculative.[21,38] Although interesting, no clear information has been gained from examining changes in simple UV/vis spectra, but ESR techniques have recently been applied to elucidate the impact of added Co^{2+} and Cu^{2+} on PVG generation of $Mo(CO)_6$[33] which show enhanced production of $^{\bullet}CO_2^-$ compared to $^{\bullet}OH$ radicals, confirming earlier speculations.[21,39] This study provides the first attempt to examine the efficacy of PVG applied to generation of fluoromethane. As predicted from the above, assistance from added metal ion sensitizers was expected, and found to be essential.

No product ions (*m/z* = 33, and 34 Da) were detected by GC-MS in the N_2 transfer gas from the GLS when solutions containing only 500 mg/L F^- and varying concentrations of acetic acid (0.5, 1, 2, 4 and 6 % *v/v*) were photolyzed for increasing periods of time (11, 22 and 43 s) during their passage through the quartz flow-through reactor. GC-MS signals were indistinguishable from the corresponding solutions of acetic acid containing no added fluoride.

The impact of Cu(II), Ni(II), Cd(II), Al(III) and Co(II) metal ion sensitizers added to the acetic acid medium containing 500 mg/L F^- was examined in the range 20 - 120 mg/L. Only the presence of Cu(II) resulted in production of a reproducible and repeatable response from CH_3F, as evident and detected by GC-MS. This was in accord with the results reported by Hu et al. who noted the specific impact of added Cu(II) on PVG synthesis of CH_3Cl.[24] All experiments relating to optimization were subsequently conducted using solutions of 500 mg/L F^- containing 60 mg/L Cu(II).

A confirmational full MS scan of the PVG products was not possible because of an insufficient concentration of generated CH_3F. However, under the GC-MS conditions used, a full scan spectrum of CH_3F chemically generated using trimethyloxonium derivatization of F^- [3,17] provided a retention time match (5.22 min) with that from the extracted *m/z* 33 and 34 Da peaks corresponding to CH_2F^+ and CH_3F^+ (retention time 5.22 min) generated by PVG sampling. Moreover, the relative ratio of intensities of *m/z* 33 to 34 arising from the PVG product are consistent with both CH_3F derivatized chemically, and with the NIST MS database EI MS spectrum of CH_3F.[25]

Optimization of CH_3F yield. Added Cu(II) concentrations of 20, 50, 60, 100 and 120 mg/L resulted in repeatable and reproducible response in GC-MS intensities (integrated peaks) invariant to its concentration. A 60 mg/L spike was selected for studies of the impact of other experimental variables. Likewise, response was determined to be invariant to acetic acid concentration (0.5, 1, 2, 4 and 6 % *v/v*), leading to use of a 2 % medium. As well, irradiation times between 11 and 43 s provided constant response.

In light of the impact of added catalysts on photochemical generation kinetics evident with Se(VI),[21,29] the effect of added titania, as both TiNano 40 TiO_2 and Degussa Aeroxide TiO_2 P 25, at concentrations of 100 mg/L was examined. No beneficial effect was detected in terms of enhancement of synthetic yields. However, in the absence of F^- in the acetic acid solution, the added 60 mg/L Cu(II) was photoreduced to produce a purplish coating on the surface of the catalyst recovered after centrifugation, likely attributed to Cu^0. A similar precipitate, identified as Cu^0, was reported by Cantarino et al. during photoreduction of Cu(II) in a solution of formic acid containing TiO_2.[40] This was not evident when F^- was present, and may suggest a stabilizing effect of complexation to prevent complete reduction of Cu(II).

Noteworthy in this study is that GC-MS signals for CH_3F generated using the Teflon wound germicidal lamp (irradiation time of 120 s) were of the same intensity as those from the quartz flow-through reactor when added Cu(II) was present (no response in its absence). This is significant, as the germicidal lamp produces no 185 nm radiation and the Teflon coil reactor transmits only 37 % of incident 254 nm radiation into the sample solution.[41] Nevertheless, such conditions are evidently sufficient for the homolysis of formic and acetic acids used for PVG experiments to generate needed $^{\bullet}H$ and $^{\bullet}CH_3$ radicals and confirm that $^{\bullet}F$ is not directly generated nor needed for the formation of CH_3F.

The PVG efficiency (apparent yield) of CH_3F was estimated from a comparative analysis of the irradiated and non-irradiated solutions of 2 % acetic acid containing 500 mg/L F^- and 60 mg/L Cu(II) by ion chromatography. Irrespective of generation conditions, the relative decrease in F^- in the irradiated solutions was consistently less than 1 %, indicative of a disappointing PVG efficiency. Nevertheless, a linear calibration function ($R^2 > 0.993$) was readily established using GC-MS response from solutions of 2 % acetic acid and 60 mg/L Cu(II) spiked to contain 0, 245, 480, 720 and 950 mg/L F^-, confirming the generation and specificity of the detected product.

Possible mechanism. Leonori and Sturgeon[21] have discussed the possible mechanisms of photochemical alkylhalide generation. Insufficient VUV photon energy is available from the quartz flow-through reactor to directly generate a $[^{\bullet}F + e^-_{(aq)}]$ radical cage complex that could yield CH_3F through direct homogeneous reaction with abundant $^{\bullet}CH_3$.[42] This is also evident from the fact that there is no detectable MS signal from irradiated solutions of acetic acid containing only F^-. Experiments undertaken with the addition of 10 - 100 mM nitrate or nitrite (as the sodium salt) to serve as aquated electron scavenging agents[21], thereby promoting the formation of free $^{\bullet}F$ from the cage complex, were unsuccessful in enhancing generation efficiency. However, addition of Cu(II) appears to initiate an alternative pathway for generation of CH_3F, possibly *via* a radical halogen atom transfer from a Cu-F complex by $^{\bullet}CH_3$ radicals[21, 43-45]:

$$Cu^{2+}_{(aq)} + F^-_{(aq)} \longrightarrow CuF^+_{(aq)} \qquad (1)$$

$$CH_3CO_2H \xrightarrow{hv} {}^{\bullet}CH_3 + H^+ + CO_2^{\bullet -} \qquad (2)$$

$$CuF^+_{(aq)} + {}^{\bullet}CH_{3(aq)} \longrightarrow CH_3F_{(g)} + Cu^+_{(aq)} \qquad (3)$$

$${}^{\bullet}CH_{3(aq)} + Cu^+_{(aq)} + H^+_{(aq)} \longrightarrow CH_4 + Cu^{2+}_{(aq)} \qquad (4)$$

Only the CuF^+ complex is considered in this scheme as it has a higher stability constant than CuF_2[46], but is less stable than the corresponding Cu acetate complex.[21] Reaction 4 may account for the catalytic nature of the role of Cu^{2+} in that it can be regenerated in the solution *via* this reaction or by oxidation with dissolved oxygen.[45] In this sense, reactions mediated by electron transfer catalysis via the two oxidation states of copper are consistent with its role in biochemical reactions.[46] Alternatively, the presence of added Cu^{2+} may by itself lead to generation of $^{\bullet}CH_3$ *via* photoreactions stimulated in the near UV-vis range, as suggested by Patra et al.[48], amongst others.

It is known that the rate of reduction of a metal center by $^{\bullet}CH_{3(aq)}$ can be enhanced by orders of magnitude when complexed by halides, leading to the direct formation of halomethanes.[44] UV/vis spectra of pertinent Cu-containing solutions are presented in Figure 1. Significant absorption by a simple Cu-aquo complex manifests itself below 250 nm; no such feature is detected at all for only F^- in DIW. In 2 % acetic acid a new feature, likely attributable to absorption by a Cu-acetate complex, is evident whereas no such feature arises for only F^- in this medium. Formation of an additional Cu-F complex when these elements are co-present in either DIW or 2 % acetic acid give rise to a strong red-shifted absorption band present throughout both the UVC and UVB regions and may account for the observation that using a simple germicidal lamp enables generation of CH_3F in the absence of 185 nm VUV radiation. Noteworthy (not shown) is the complete absence of such a UV/vis absorption features in comparable solutions of the other tested metal sensitizers, making a unique case for the efficacy of added Cu(II). It was verified that these absorption bands were not due to the presence of any adventitious nitrate, which exhibits intense absorption in this same wavelength region, as none was detected in these non-irradiated solutions by IC; furthermore, sulfate does not generate any absorption features in this wavelength region.

CONCLUSIONS

This study presents the first evidence of photochemical synthesis of fluoromethane. Intervention of Cu(II) as a metal ion "sensitizer", suggesting a radical halogen atom transfer synthesis mechanism, appears mandatory for the reaction to proceed. Noteworthy is that application of a standard germicidal lamp having little output below 250 nm competes favorably with the performance elicited from a flow-through quartz reactor operating in the VUV region. Clearly, homolysis of acetic acid, achievable with the latter lamp, supports the reaction in the presence of Cu(II).

As the current yield of the PVG process is disappointingly low (<1 % efficiency), the methodology is not suitable for augmenting sample introduction efficiencies for atomic spectrometric techniques to enhance detection power. Further work remains to explore this system, potentially making use of the unique properties of metal oxide framework catalysts to enhance the synthetic yield.[49,50] Photocatalysts, in combination with Cu(II), may enable synthesis of CH_3F using only visible wavelength radiation[51] in the presence of acetic acid for efficient generation of $^{\bullet}CH_3$ by the photocatalyst and abstraction of fluorine from $CuF^{+}_{(aq)}$ complexes.

Conflicts of interest

There are no conflicts to declare.

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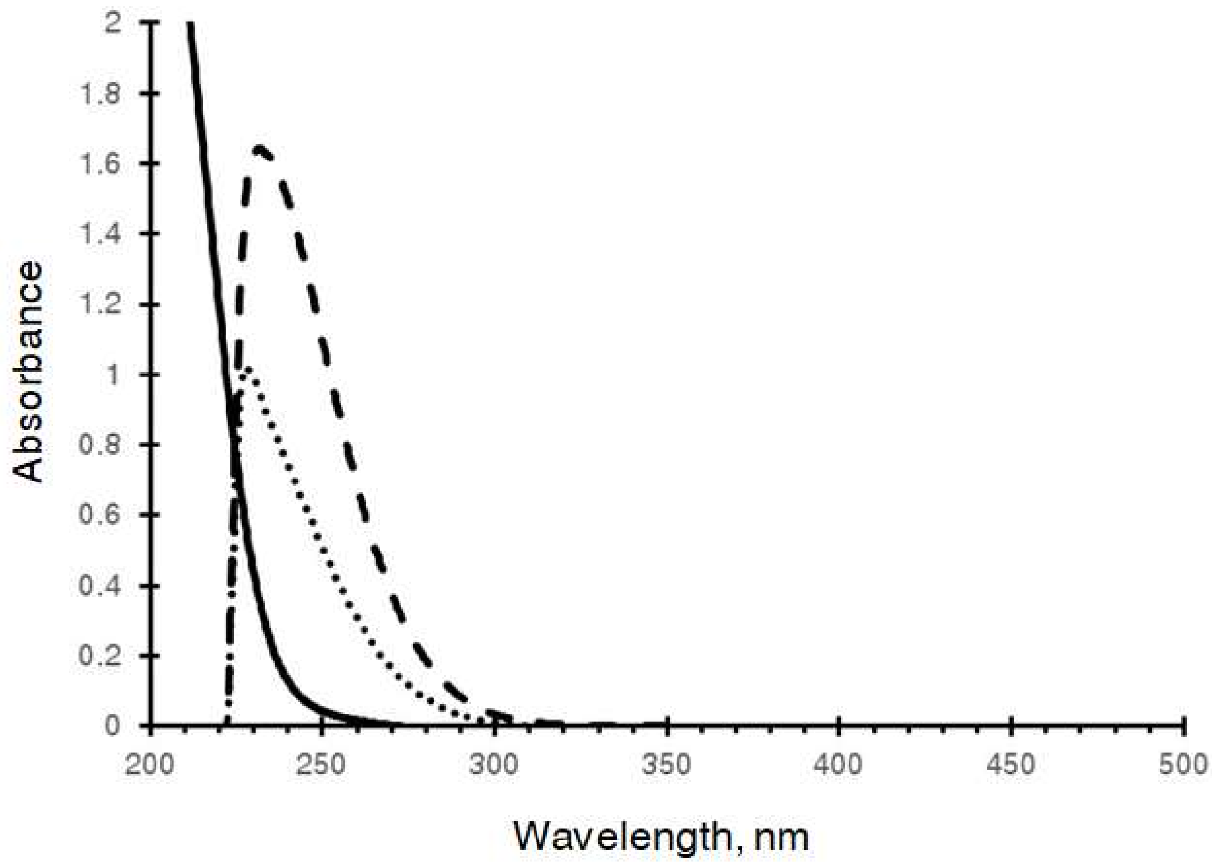

Figure 1. UV/vis spectra depicting: ——— 60 mg/L Cu(II) in deionized water (DIW); ········· 60 mg/L Cu(II) in 2 % acetic acid; – – – mixture of 60 mg/L Cu(II) in the presence of 500 mg/L F^- in 2 % acetic acid. Reference spectra in each case was the common solvent, i.e., DIW or 2 % acetic acid