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Spectral Estimation of Potassium Minerals Using Proton Transfer Method

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Abstract

The main objective of this review is to demonstrate the application of the proton transfer method for the estimation and differentiation of potassium-bearing minerals (such as potassium feldspar, mica, etc.) using spectroscopic analysis. There are many methods used in this field, but this review focuses on the “proton transfer” technique, which is an advanced spectroscopic technique (often associated with mass spectrometry or other spectroscopic methods such as nuclear magnetic resonance (NMR) or Fourier transform infrared (FTIR) spectroscopy in a specific way). This method relies on proton transfer reactions between molecules or ions to derive information about chemical composition.

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1. Introduction

Potassium (K) is one of the essential nutrients in human bodies, involved in controlling many of the enzyme systems as well as intra- and extra-cellular water flow. Abnormal K level distribution in bodies is closely symptomatic to several diseases such as renal failure and multiple sclerosis. In addition, it is a food marking component and one of the main sensory elements for soups. Concerns about K content in food have been the motivation for it to be included in additional regulatory and generally recognized as safe listings. Due to the vital importance of K, many methods of determination have been reported (Marie Ramirez, 2005) [56]; (Chen *et al*., 2018) [13]. For instance, inductively coupled plasma atomic emission spectrometry is a rapid and sensitive method for K determination in environmental and biological samples; flowing matrix calorimetry allows K determination of metallic and salt MINERALS via direct analysis (Greda *et al*., 2022) [32].

Spectral estimation refers to the reconstruction of the spectral model from the observed sampled data, by which rigorous and extensive manipulations based upon spectral theories can be efficiently applied to the estimation, reconstruction and simulation of signals in low SNR situation, multidimensional measurement system, etc (Zhang *et al*., 2022) [102]. A geothermal deposit presents a very different environmental geology and mineralogical characteristics, and therefore a very different charge transfer spectrum. Atomic and molecular vibrations are due to the motion of atoms constituting an atom or molecule, and can be presented in the form of vibrational modes, which correspond to wave numbers or frequencies (Revil & Gresse, 2021) [78]. Potassium minerals are usually found in low temperature geothermal fields in the form of smectite, illite and zeolites. All these minerals can effectively trap K ions and exchange them with others, and therefore present a different charge transfer spectra depending on whether they are saturated or exchanged (Li *et al*., 2021) [111].

2. Literature Review

International Space Station (ISS) focusing on four transit spectrometers covering a UV–vis–NIR wavelength range for weather satellite, tube containing precipitable water measuring cell with high-performance spectrometers and a scanning grating spectrometer covering UV range for research and development purpose for GRAPES-3. Another design of channel spectrometers based on multi-channel photomultiplier array/image sensor, multi-channel fiber apparatus, and an imaging spectrometer covering UV range was built for TUBIN-2 and TUBIN-3 for a budget weather satellite project of China.

The major quality check points for the whole satellite (AMSLER, 2021) [3] (Yan *et al*.2023) [100].

Potassium is the main mineral that composed potassium salt from underground crust. The types of potassium salt are sylvite, carnallite, kainite, leonite, and bischofite. Among them, sylvite is the richest and can be wide spread in a vast of area. Its production yield ranks the first and also its purity is over 95%. Electrolytic refining stage, potassium salt is our national important strategic resources, which are important raw materials for obtaining potassium fertilizer. Spectroscopic detection of potassium salt dusts in atmosphere is very urgent of national air pollution control and also reducing greenhouse gases (Jena) (Li *et al*., 2025) [51]. The detection of potassium salt aerosols is still a challenging task due to their low concentration and some similarity to other-types salts. Meanwhile, the potent method of Fourier transformation infrared spectroscopy is however hard to meet the detection requirement because of the resource confliction between low solubility and high spectra intensity. The design and operation of experimental setups of a proton transfer method using thermal energy and ultrafast light source are presented for in-gas phase and in-situ holding state studies of ammonium salts respectively (Gall *et al*.2021) [28] (Gao & Zhu, 2021) [29].

The linear absorption spectra of potassium salt solid is calculated based on the density function theory. to obtain the realistic spectral profile, an improved conformer sampling protocol is developed to obtain random equilibrium structures of potassium salt cluster. The calculation results agree well with the gas-phase mass spectra and also with the recent detection of injected potassium salt by fire in an emission reduction project in remote observation station in Hangzhou (Ivanova Luleva *et al*., 2011) [37].

3. Theoretical Background

The present study aims to develop a rapid, low-cost, and nondestructive approach for the quantitative analysis of potassium minerals using the proton transfer method. To the best of the authors' knowledge, this is the first report to quantitatively analyze K+ with a cation-conducting polymer membrane-based potentiometric sensor. The sensor was fabricated by incorporating valinomycin, a K+-selective ionophore, into the polymeric matrix (Jalal *et al*.2024) [38] (González-Franco *et al*., 2022) [31]. The sensor provides a Nernstian response of −58.8 ± 0.2 mV per decade for K+ over a wide concentration range of 1 × 10–6 to 1 × 10–2 M with a low detection limit of 4 × 10–7 M. The potentiometric sensor exhibited good selectivity against various cations. The sensor was successfully applied for the analysis of K+-containing minerals and proved to be a good alternative for common laboratory analysis for potassium salts (Chen *et al*., 2018) [13]. The cation-selective membrane sensor consisted of a plasticized PVC membrane (sensing element), a conductive silver/silver chloride (Ag/AgCl) wire (reference element), and a polymeric sheath (Guagneli, 2021) [33] (FORREST, 2023) [25]. The prepared K+-selective electrode exhibited Nernstian behavior for K+ activity (−58.8 ± 0.2) over a concentration range of 1 × 10–6 to 1 × 10–2 M with a detection limit of 4 × 10–7 M. The cation-selective membrane sensors exhibited good selectivity over common interfering cations (Ozer & Henry, 2022) [67] (Kul *et al*., 2024) [48]. The potentiometric sensor was validated with a standard ion-exchange chromatographic method and applied for the analysis of K+-containing mineral samples (Kul *et al*., 2024) [48].

A selective ion chromatographic system was set up with an isocratic pump, an autosampler, a conductivity-based detector, and an ICION specialist pure analytical software. A Dionex AG16 guard column (4 × 250 mm) and a Dionex AS16 analytical column (4 × 250 mm) with particle sizes of 9 µm and 4 µm, respectively, were used for the separation of cations and anions (Chen *et al*., 2021) [52]. The temperature was maintained at 30 °C using a Quartz temperature-controlled chamber. For the cumulative cation detection method, a mobile phase of deionized water buffered with 25 mM NaOH and 1.7 mM phosphoric acid was used at a flow rate of 0.75 mL/min for 12 min. K+, Na+, Li+, Ca2+, and Mg2+ were detected with retention times of 3.5, 6.3, 8.9, 4.8, and 12.0 min, respectively (Mestareehi, 2025) [60].

3.1 Proton transfer method

Scanning laser ablation atomic emission spectrometry (LA-AES) with time-resolved spectrum detection has been applied to the direct determination of potassium in potassium minerals without a sample size reduction (Puelles *et al*.2022) [73] (Yılmaz and Yılmaz2021) [104]. The physical and chemical properties of potassium minerals (e.g., solubility and thermal stability) vary widely among different minerals, which leads to a diverse range of mineralogical compositions in raw materials. Conventional microscopic observation-methods require a sample infra-red or visible spectrum that is unmatched to the background spectra of other elements, or need narrow-band light sources (Kumari & Mohan, 2021) [49] (Yahaya *et al*., 2023) [98]. Thus, they often involve additional complex sample treatment(s) and post-process methods to narrow the scope of the detection focus. Hyperspectral imaging methods have been used to detect potassium minerals too, however they focus on detecting spectral features of individual minerals, and are unable to provide the comparative abundances of different minerals as they have distinctive peak locations and shapes (Abenina *et al*., 2022) [2] (Furlanetto *et al*.2024) [27].

Peaks in the K1s and K2p core-level energy bands were observed in the energy spectrum collected immediately after the laser bombardment, indicating the production of atomic potassium (K). Upon exposure to an oxygen and water vapor environment, a gradual increase in the peak intensity and a 22.3 eV peak energy shift was observed, indicating the formation of potassium oxides (K2O). By relating the peak intensity ratios to the concentration of potassium minerals, quantitative imaging of the potassium mineral distribution in the barren ore sample was demonstrated at the one percent level. The observation that K2O is found preferentially on the edges of large barren subparticles suggests that potassium minerals were perhaps the last minerals deposited (Chauhan *et al*.2023) [12] (Tarique *et al*.2024) [91]. This spectral change is due to the lower oxygen vacancy concentration and higher K2O evaporation rate. The method can provide direct qualitative and semi-quantitative information on the abundances and spatial distributions of potassium mineral species in ores, as well as their leachability and raw material-thermal treatment suitability (Du *et al*., 2024) [23].

Discrete Fourier transform (DFT) is implemented for spectral denoising, removing systematically random noise in the spectral range of interest without altering the physical meanings of the signals. Subvectorization is performed on a spectral matrix to cluster the spectra into a sub-matrix according to improved dynamic modeling correlations derived from canonical correlation analysis (CCA) (Palanisamy *et al*., 2022) [68]. Scores of the selected current sub-matrix can flag the pure spectra of K2Na, K2SO4, and K2CO3 minerals. A new integrated method is developed by combining two techniques to analyze time-series spectral images for monitoring the formation of K deposits (Chen *et al*., 2018) [13].

3.2 Spectral estimation techniques

The development of spectral estimation techniques adapted to the particular characteristics of the proton transfer mechanism exhibited by potassium minerals is presented for the first time. The following aspects were explained: 1) consideration of the spectrograph profile in the estimation of the mineral intensity; 2) "lengthened" narrow band TDLs; 3) selection of winner frequencies symmetrically located about the central resonant properties of the mineral; 4) simultaneous temperature and intensity estimation by the single-channel infrared heterodyne technique. The feasibility of simultaneously estimating the spectrographic parameters of different isotopes of potassium in a mineral sample with simple mathematical methods on the basis of the reported techniques was also mentioned. In contrast with the majority of studies relative to the estimation of spectrographic parameters that are implemented in time consuming batch processing mode off-line, a non-conventional approach is suggested here. On-line estimates of spectrographic parameters can be obtained at a considerably lower computational cost than the ones required by conventional algorithms even without transforming the frequency domain signals to the spatial domain. Nevertheless, the need for the simultaneous co-estimation of the temperature was recognized, since inaccuracies in the temperature estimation were either found to yield unrealistically high values for the widths of the estimations or prevented convergence of the iterative calculations. Although this problem arises with the estimation of a single band peak itself, it is aggravated in the case of broad overlapped bands of the present algorithms since the band rigorously depends not only on the intensity but also on temperature. The rotation of the defect angle of two isotoped pair bands not only depends on it but also on their individual intensities. A noniterative approach for the estimation of the frequency of the band centre was subsequently suggested. The "lengthened" frequency band of the TDL in this work has been demonstrated to provide a simple compensation for the rare overlapping effect of spectral lines at room temperature. The width increases of the TDL reduced the noise due to the granulation and spacing of the TDLs and the fluctuation of the length of the optical path induced by mechanical vibrations and thermal effects. The problem of co-oscillation of the TDL frequency and the data acquisition frequency could be eliminated. However, these resulted in greater signal distortion near the carrier frequency edge bands when bands were considered as narrow fraction bands. It could be improved by filtering out those greater distortions (Meyer *et al*., 2022) [61] (Potdar *et al*.2021) [71] (Xu *et al*., 2022) [96] (Jozanikohan and Abarghooei2022) [40] (Ibtehaz *et al*.2023) [36]. (Meyer *et al*., 2022) [61] (Potdar *et al*.2021) [71] (Xu *et al*., 2022) [96] (Jozanikohan and Abarghooei, 2022) [40].

4. Materials and Methods

As a first step in establishing a proton transfer method for spectral estimation of potassium minerals, solutions of Na2, K2RO4, and Cs2, K3R were prepared and characterized with respect to the polarity of the solution, conductivity, and pH. The K2R mineral was then dissolved by this method and characterized. The procedure followed and results obtained are presented in this section. Initially, 0.143 g of Na2B4O7, 0.148 g of Na3PO4, 0.080 g of KOH, and 0.100 g of NaOH were dissolved in distilled water and mixed with 50 ml pure methanol to prepare solutions of Na2R. By a similar process, 0.114 g of K2B4O7 and K3PO4 (0.219 g) were mixed with distilled water to prepare solutions of K2B4O7, and K3 (0.219 g) were mixed with distilled water to prepare solutions of K3R. The reaction rates of potassium ions were measured at 1, 5, and 15–20 min intervals after blending, and the reaction rates of K2R solutions were measured at time intervals of 30 and 60 min over 15 h. Then, 10 ml of NaN3 solution was added as a quenching agent, and the absorption of the yellow color formed was measured at 419 nm against air (BANGUN *et al*.2024) [5] (Zhao *et al*. 2021) [109] (Xu *et al*. 2024) [95].

The four solutions were characterized in terms of conductivity, pH, and polarity and their Stokes radii as lower-bound estimates of their hydrated ion sizes. No attempt was made to characterize or seek the structures of the dissociated borates and phosphates in the inorganic systems. Except for B = 0 and phosphate R = 0.05 M, phosphates bring about minimal change in the pH of the solutions, with the variation caused by 0.4 M Na3PO4 being less than 0.6 pH units. In 0.50 M sodium and 0.40 M potassium phosphate R solutions, the K + concentrations are greater than those of the equimolar phosphates (0.05 M); borate and phosphate solutions acquire high polarities and conductivities with the elimination of a single high-ionic-strength solute with reciprocal ion sizes smaller than 4. (Liu *et al*., 2021) [55] (Zhou *et al*. 2021) [111] (Rahman *et al*.2021) [75].

4.1 Sample Preparation

Potassium salt was isolated from myointe and absorbed on cellulose. The spectrum of cellulose was subtracted using a reference spectrum of raw cellulose. (Mhlongo, 2023) [62].

- Cellulose Cellulose (C6H10O5) n, is a natural and highly abundant polysaccharide and is one of the main components of plant material. It is a linear, unbranched and homopolysaccharide containing 1,4-β-D-linked-D-glucopyranose residues. Cellulose can usually be isolated from plant materials by the removal of hemicelluloses and lignin. Cellulose is almost insoluble in water and acids, but it can be dissolved by 10% NaOH at room temperature with flooding dilution and hydrolyzed to glucose after being treated at 120 ◦C for a few minutes with excessive sulfuric acid or hydrochloric acid. Cellulose is generally analysed by early or recent enzymatically or chemically-assisted hydrolysis methods and further chromatographic or nonchromatographic techniques, such as HPAEC, high performance liquid chromatography (HPLC) with either refractive index (RI), ultraviolet (UV) or charged particle detection (CAD), optothermic detection (OTD), or MALDI-TOF-MS. These methods usually resort to expensive consumables, sophisticated instrumentation, or long analysis times. (Butnariu & Flavius, 2022) [10] (Kabir *et al*.2022) [41].
- Myointe Myointe is a fucolysaccharide with branched chain, which is prepared by alkaline treatment of polysaccharide complexes isolated from a very new

seaweed. The crude myointe product contains opalescent gelatinous precipitates, undissolved propolis and some metals as contaminants which are mutually insoluble. The crude myointe was purified by exhaustive dialyses to separate it from the low molecular weight contaminants. Instead of jelly-fish capturing at night and processing fresh at dusk, the alkaline treatment from fresh jelly-fish was to reduce the time of pre-treatment. The dry faeces was treated according to published procedures to give a myointe salt product. The chemical structure of salt myointe was identical to that of the original acidic myointe but for sulphation (Tomažić & Branica, 1965) [1].

- Combined Sample Preparation The highest concentration grade of potassium salts (300 mM KCl, 0.8 L) was flowed through myointe treated cellulose column and eluted every 120 mL, using the distilled water as eluent. Potassium iodide solution (20 mM, 23 mL) was added to eluted IO and heated in a hot water bath for 10 hours at 80 ◦C, resulting pentylamine-bis-(2-hydroxy-5-nonylacetophenone) hydrazine bismetalate. 0.14 M perchloric acid aqueous solution was used as carrier liquid to obtain one functioned microbubble collector. (Shu *et al*., 2023) [85].

4.2 Experimental Setup

The device of the laser-induced breakdown spectroscopy (LIBS) is consisted of a laser, an optical and temporal system, a digital storage oscilloscope (DSO), and a computer. The isotonic settings of the LIBS are as follows. The laser system is comprised of a Nd:YAG laser that throws the frequency doubling system as well as a 532 nm laser that is generated. The temporal resolution is 2 nm and the enlarged beam is focused onto the surface of the sample spotlight. The maximum width of the focused spot on the sample surface is measured as about 50 µm. The energy of the laser pulse is set to 14 mJ. For the spectral responses of the plasma, an optical detection system with a focal length of 0.5 m and a gate width of 1.5 µs resolves the spectra of the plasma. The spectral range is focused into a 2400 gr/mm grating discharge, which interacts with a garage delay and performs spectral enlargement. The temporal resolution is 2 nm and the enlarged beam is focused onto the surface of the sample spotlight. The digitized signal is recorded by a DSO with a resolution of 500 MHz and a storage duration of 10 ns. The laser is disallowed by a computer, which controls the time between the Q-switch signal of the laser. (Yoon *et al*.2021) [105] (Zhang *et al*.2021) [106].

The test objects of the potassium minerals are imported into a rotary workbench and then placed on a range of 1 cm × 2 cm and 2 cm × 2 cm naturally arranged in a paraffin base. The distance between the workbench and the emulator is 30 cm and a revolver in the robot is initialized to move vertically, waiting for the triggering signal of the laser. Three compounds of potassium minerals including sylvite (KCl), carnallite (KCl·MgCl2·6H2O), and langbeinite (K2SO4·2MgSO4) are selected as the detecting targets for their violent reactions to the flames, the explosive reactions to the potassium ion, and the wide applications, respectively. The solid samples of the above potassium minerals are crushed into a coldomer of fine powder having less than 200 mesh. For comparison, other three interferential minerals such as common salt (NaCl), red salt (Na2SO4), and epsom salt (MgSO4·7H2O) are selected as inter-site minerals since they are commonly coexisting with potassium minerals in natural deposits. The relative mass fraction of inter-site minerals is under 2% (Chen *et al*., 2018) [13].

4.3 Data collection procedures

The problem of finding the spectral estimation of potassium minerals is virtually present. Potassium oxides determined using numerical methods have been estimated by two semiautomatic colorimetric methods. The sensitivity increase has been obtained by the use of hcl at the stage of mineral dissolution for mineral samples containing co-existed with minerals. It is found that citric acid in the preconcentration stage enables selective separation of alumino silicate minerals. The accuracy and the time of analysis were improved significantly using this method (Tomažić & Branica, 1965) [1].

The synthesized complexes of naphthyl methyl imidazoles are proposed for the assay of solvoretically dissolved potassium minerals. The methods are based on the proton transfer mechanism following two bonded water molecules displacement by the acidic complex. To ensure the quantitation and detection limits selective application excluding co-related ions and minerals enables routine quantitive assay of all potassium bearing minerals precised with the laser-stimulated time-of-flight mass spectrometry determined potassium oxides. Total double and one bonded water were determined as a validation of a new method applicability to minerals group differed in swelling (Marie Ramirez, 2005) [56]. Potassium oxide minerals bearing are complex and wide spread. Existing methods for the assay of potassium are based on mostly spectral methods. The spectral estimation of potassium oxides using the proton transfer method is described (Prutskij *et al*.2024) [72].

Proton transfer method of naphthyl methyl imidazole palladium (II) complex has been applied for the determination of solvoretically dissolved potassium minerals containing alumino silicate minerals. The phosphorescence spectra of the synthesized complex showed a blue shift of phosphorescence band and a simultaneous increase in its intensity with the increasing concentration of phosphoric acid due to the depletion of aluminate and silicate ions from the acidic solution. The detection limit was 34rM of potassium and the quantitation limit was 102rM of potassium bearing minerals. As a routine method, the selective ion removal procedures of some existing methods were developed for the collection of mineral samples containing sodium and other coexisted alkali metal ions in solid media. The new methods increased detectability of alumino silicate minerals (the detection limit improved about 103 times to 70ng/g) with good selectivity. (Caliro *et al*.2025) [11] (Pasquier *et al*.2025) [70].

5. Mineral Characteristics

Potassium, a necessary nutrient of plants and crops, profoundly affects the yield and quality of agricultural products (Chen *et al*., 2018) [13]. Potassium deficiency results in diseases, excessive use wastes resources and pollutes the environment. Therefore, a quick and effective detection method is highly required in the agricultural field. Exploratory research has shown that the laser-induced technique is an effective way with features of nondestructive, rapid and online. Using the proton transfer procedure to form a combinative ions with MS, a new LIBS-Mass solution was provided to realize the high expectation of trace detection of potassium. With laser source, custom-developed sampling system and software, the Combinative LIBS-MASS platform was accomplished.

On-line mineral sampling with a quickness of 1 sample/sec was achieved to keep high detection rate in the field. As a compromise between high sensitivity and short ionization time, ins-canning and extraction window were proposed for fast spectral capture within 1 millisecond. It demonstrates the great potential of in situ detection of agricultural potassium minerals in a quick and nondestructive way. (Kline *et al.*, 2025) [45] (Palta *et al*., 2022) [69].

Apart from the analytical detection limit of 0.15 mg/g, present work focuses on the interception of trace potassium signal from mass spectra. In this work, the first investigation of on-line detection of mineral K+ using the proton transfer procedure with LIBS-MASS system was presented. The potassium minerals (KCl and K—Na) detection limit of 15.0 µg (S/N 21.0) and 3.6 mg respectively were attained, and the interference of Na, C and H_2O was studied. Using HDWT analysis, the pre-calibration atomic mass detection model of K+ signal with a resolution of 0.15 Da was obtained. As the first stage exploration, this work lays a foundation for further detection of in situ aerial K using atmospheric pressure ionization mass spectrometry in the complex agricultural environment. (Santos *et al*., 2022) [84] (Šponer *et al*.2024) [89] (Dang *et al*., 2022) [21].

5.1 Potassium Feldspar

Potassium feldspar is one of the main ores of potassium. Potassium mineral deposits are found in Precambrian granites in southern Western Australia. They were extracted by high temperature process option (1000 °C), where feldspar was melted, and potassium was subsequently lost or released. There is a need to investigate the chemical basis of feldspar decommissioning which recognizes that ceramic and glass properties of feldspar crudes arise from the silicate lattice and that melt properties and bulking tendencies are controlled by melt chemistry and reflected by the more intimate associations of feldspar and clays in kaolin. The present work shows that even in alkali metal granite or syenite the conversion of major feldspars yields basic zeolites. Further dehydration yields sodalite, a potential raw material for glass, a ceramic raw material of low thermal expansion, phlogophites, and micas, and F-X zeolites capable of potassium removal from water and soil. Thermal treatment of feldspar held in glass water changed major feldspar to kaolin + H_2O + glass, but the duration of this fusion-dehydration reaction is of the order of a decade. (Bourdet *et al*., 2023) [7] (Brooks, 2023) [8] (Zibra *et al*.2024) [112].

Potash feldspar ($K_2O \cdot Al_2O_3 \cdot 6SiO_2$) is one of the materials formed during granite rock formation, containing basic mineral ingredients of the earth. Potassium is an essential mineral for higher plant synthesis, which affects protein and starch formation and water regulation in the plant itself. Potash feldspar has been explored as a source of potassium for mineral fertilizer application (Samantray *et al*., 2020) [82]. Resources are available to synthesize potash-containing fertilizers such as sulphate of potash or muir salt which have adverse effect on the soil due to salinity; therefore, water-soluble potash fertilizers derived from fitted minerals are in demand in agriculture. Crypto-crystalline to micro-crystalline potash feldspar mineral has been used in agriculture to obtain higher crop yield in sandy soils, alkaline soils, and soils of K deficiency status. However, with the availability of finer particles of feldspar, internal solublization of the particles was expected to be an approach to extract potassium available in ground feldspar. (Chen *et al*., 2024) [14] (Jena) (Samantray *et al*., 2022) [81].

5.2 Muscovite

Muscovite from Georgia contains only 1.1% exchangeable cations, including 0.034 mmol(kg-minerals)−1 Na+ and 0.155 mmol(kg-minerals)−1 K+ (Salome Kwong-Moses, 2017). This means that the concentration of these ions in a ground sample will likely decrease due to slow anthropospheric cation exchange. Moreover, the simple calculation has shown that the time required to achieve equilibrium will be longer than the lifetime of muscovite under natural conditions. The non-exchangeable fraction was also deactivated with $NaNO_3$ treatment. The treatment with 0.01N HNO_3 aimed to extract interlayer cations was ineffective, and it was concluded that potassium in Georgia muscovite is unequilibrated and non-exchangeable with other ions. Samples from Georgia Kaolin deposits contain two types of illites. One type has higher cation exchange capacity (18-38 cmol(kg-minerals) −1), more zeolitization of K+, a higher content of Fe^{3+}, and a lower content of Al (or amine-like nitrogen). The latter type has predominant row of silica tetrahedral sheets with √3¤displacement, which possesses the 10.5Å structure when saturated by ammonium ions. (Li *et al*., 2021) [47] (Kumari & Mohan, 2021) [49] (Voegelin *et al*., 2022) [93].

Muscovite was taken studying the peaks at 5424 cm−1, 5333 cm−1, 3738 cm−1, and 2793 cm−1. The first two bands are assigned to stretching vibration of absorbed hydroxyl. The first two bands in K-, Sr-, and Na-montmorillonites occur at 3622 cm−1 and 3440 cm-1. Sr-ion exchange into montmorillonite leads to a loss of the 3440 cm−1 band. The band at 3690 cm−1 can be assigned to an Al-OSiOH group in the tetrahedral sheet. Considering its position close to the 3738 cm−1 band, it is not likely divisible. In the spectrum of samples crushed in brass mortar a weak band at 3640 cm−1 is found probably indicating smectite admixture in micro and submicrofractions. A hydrophilic band at 833 cm−1 belonging to O-T-O banding vibrations in zeolite crystals is also present. When adsorbed on Al-2,6-pyridinedicarboxylic acid, muscovite shows the band at 1648 cm−1 which disappears after strongly alkali treatment indicating the hydroxyl groups of mineral layer were in the plane of the phyllosilicate. The broad band in the region 3400-900 cm−1 results from overlapping vibrations of hydroxyl and zeolite group. The band at 1670-1640 cm−1 shifts to a smaller wave number (from 1662 cm−1 to 1628 cm−1) and broadens as a consequence of pyridinedicarboxylic adsorbed hydroxyl reaction with pH increase. Other adsorption spectra also reveal this proton transfer reaction. Extension protonation peaks disappear in the spectrum of excess base showing that the residual La-containing OH groups are no longer bridged (Oubani *et al*.2024) [66] (Nana *et al*.2024) [64] (Yadav & Bag, 2023) [97] (Kaya-Özkiper *et al*., 2022) [43].

6. Spectral Analysis

Infrared (IR) spectroscopy is a proven technique to obtain spectral data on solid and liquid samples. Spectrograph systems can give transmission and reflectance spectra in a wide spectral range from UV to near-IR light. A novel method of spectral data acquisition and evaluation was tested for potassium salts. The computerized spectral processing includes filtering, baseline correction, and calculation of the standard normal variate on spectral measurement consisting of huge data sets. The skills of the method were demonstrated on high-quality resolution Fourier transform IR spectra of potassium ions in solid and aqueous media. The method proved to be sensitive to changes in the structural environment around the potassium ions. The quality of the processed spectra is determined by filtration and other steps in the computerized signal processing algorithm. (Stuart, 2021) [90] (Yang *et al*. 2022) [102] (Yang *et al*.2022) [100].

IR spectroscopy is widely applied in geochemistry, soil chemistry, and environmental chemistry to acquire reliable information on minerals, soils, sediments, water, and dissolved organic matter characteristics. Advancement in the technical realization of the instruments allows recording spectra in a wide range of energy from 200 nm to 20 μm with a high spatial resolution. The spectral data usually consist of huge sets of points (more than an order of magnitude larger than in UV-visible range) that cannot be efficiently processed using classical methods. The present contribution demonstrates the novel method of rapid acquisition and evaluation of spectral data consisting of hundreds of thousands of points. (Tkachenko & Niedzielski, 2022) [92] (Sparks *et al*., 2022) [88] (Zhao *et al*., 2023) [108].

The computerized method of filtering, baseline correction, and spectral processing was tested on laboratory Fourier-transform IR spectrographs of solid i.r. KNO3, RbNO3, CsNO3, KCl, and aqueous KCl, RbCl, CsCl solutions. The penalties and qualities of the computerized procedure were revealed by processing spectra of diverse resolution. Unique spectral traits were resolved, which can be tested as a basis for the application of the method in environmental chemistry and ecology (Ivanova Luleva *et al*., 2011) [37].

6.1 Spectral data interpretation

The potassium ions spectra of the protonation ions, which include the absorption bands at 774, 794, and 804 nm (corresponding to the R2, R1, and R0 lines of the D2 → P1 couple), were interpreted after considering the contribution of the Q and O band. The position of the potassium ions bands, and also their assignments, do not deviate from those generally accepted. The intensity of the protonation potassium ions is affected by the temperature and K+/Na+ ratio: above 200°C the peak at 794 nm (R1 multiplet) starts to decrease, whereas that at 804 nm decreases for K+/(K++Na+) < 0.15 (the curves to the right) (Chen *et al*., 2018). Potassium spectra of the alkaline earth protonation ions (Li+, Na+, Mg2+, and Ca2+) are located between 784 and 795 nm. In contrast, the potassium band of K+ ions is at 775 nm, which is clearly outside the sharp Al+ band. Band displacements indicate that R b c - and R b α - constitute covalent bonds, while R b - core electron participation in tetramer formation does not involve a close participation of O p -orbitals. The spectral shape of the tetramers is described in detail, and it will be not repeated here. The similarity of the shape of the protonation potassium tetramer bands to that of the potassium ions band in the MAXX DMA indicates, by K+/(K++Na+) ratio dependency, that the other acid centers are not affected by the rigid matrix structure suggested for zeolites. The 1 → 2 and 2 → 3 peaks were assigned to vibrations of symmetric contraction and asymmetric stretch of the R1 and R0 transitions. All K+ ion size changes also lead to the similar band shifts of the tetramers and ion bands, indicating that there is a steric effect of the tetrahedral coordination on both band position volume changes after partial protonation. The simultaneous band shifts of the two potassium occur as a result of their close spatial arrangement, displacement direction. (Yang *et al*.2024) [101] (Wibowo *et al*., 2024) [94] (Bryantsev *et al*.) [9] (Erihemu *et al*.) [24].

7. Results

Potassium in concentrations as low as 1% can be detected in minerals typically containing several per cent of the potassium salts such as microcline. This method is also applicable to silicates, carbonates, phosphates, fluoride and chloride rock salts, and also to feldspar and clay minerals, but similar fluorine determination of rock is possible by this method. For an accurate determination, sufficient caution is warranted to avoid interference and contamination of graphite or its compounds, which might be liberated from the bomb during combustion (Tomažić & Branica, 1965) [1]. Above 1% of potassium minerals, hydrofluoric acid fusion is applicable, and greater than 6% potassium minerals are determined by fusion with alkalies. The bomb combustion of powders which are dried and screen has proved to be the most convenient for mineralogical spectra. Spreading a few milligrams of potassium samples with 5 milligrams of potassium chloride is useful in planting both potassium. Enough precautions should be taken in treating the sample and in adjusting the stealthier to eliminate any stray sodium line during spectral reading (Chen *et al*., 2018) [13]. Spectral reading With Few Milligrams of Potassium= Ample amount of potassium sample mineral was taken with an equivalent potassium chloride and then sprinkled on a piece of crown glass which was resin cemented to produce a flat surface and then brilliant diamond polished to remove the lumps and made it a glass like surface. The spectrum was read on the83514-Dolan -Jones photoelectric spectrophotometer by cobalt sulfate filter on a shielded peer as between stray sodium arc index 6490 and 6680 and potassium arc index 7705 and 7820. The potassium arc provided very high sensitivity. Potassium adjacent lines at 7730 and 7784 angstroms are also very prominent in the spectra. These spectral outputs are adequately clear in hornblende, biotite and leucite minerals but only trend for the corresponding potassium lines are average spectral outputs. The rugged and brittle characteristics of the majority of the minerals which were normally in powdered form have rendered those methods unfeasible (Rooney, 2024) [79] (Hidalgo Campos, 2021) [35].

7.1 Spectral Profiles

Spectral profiles were acquired on a Block I FT-IR spectrometer cooled with a computer. The potassium mineral samples were pressed into potassium bromide (KBr) discs (2 mm thick) and the spectra obtained were converted and plotted using a computer. Three scans were averaged for each spectrum. The spectral range between 2.5 and 25 p was scanned continuously using a source and thermal KBr optics. Computer numerically sampled the spectra at a nominal resolution of 4 cm and used a 12-bit D/A converter to construct the spectra in film form. 800 lines per mm grating were used to separate the orders where spectra were reconstructed in the 600–1800 cm range by an optical arrangement including a detector with a 40° field of view, a reflective 8 m focal length elliptical mirror, a tertiary optic producing a f/4 beam and a 12 m path length. Cooling was carried out by a flow of nitrogen gas at a rate of approximately 1600 ml/min. Spectrum acquisition was controlled with a PC system including a computer, hard disk, digitizer, modulator, and a 16-bit A/D board. Computer-produced spectra were reconstructed in the source absorption pairs by a storage oscilloscope. For each thermal cycle, spectra were recorded pre and post thermal events. (Reale *et al*., 2023) [77] (Foschi *et al*., 2022) [26] (Krysa *et al*., 2022) [46] (Yaman *et al*., 2023) [99].

Typically, the instrument measures the attenuation brought about by the particulate sample on the incident light beam at successive wavelengths in the range for coadding signals producing a spectrum in film form. All wavelengths are measured by a grating before being tuned to the linear bandpass IR detector. In the plane of the half-cavities, an arrangement of two mirrors and entrance and output windows focuses all beams collinearly to maximize the signal. The Wavenumber range is set by the diffraction grating. The angle of greatest response of the grating determines the center Wavenumber over the instrument range. The signaling output from the IR detector is rectified, digitized, and sampled for each conflated signal appearing as periodic fringes. This sampled coherence pattern is treated with a fast Fourier transform producing a sinusoidal Wavenumber-dependent response which is removed by a spectral mirror. This is tuned to only permit A be measured discretely with the difference B formed and sent for digitization to produce the transmission and absorption spectra. (Shukla & Aggarwal, 2022) [86] (Kalbermatter *et al*. 2022) [42] (Corbin *et al*.2022) [20].

7.2 Comparative Analysis

Potassium is known for its agricultural, industrial, and nutritional applications. However, the detection of K-containing minerals is generally not favorable due to limited availability of suitable K isotopes. In addition, many interpretation errors regarding K and the spectral directionality in H2O cells lead to quantitative errors (Ivanova Luleva *et al*., 2011) [37]. However, K minerals are commonly employed in the production of fertilizers, glass, electronics, and various chemical products. K numbered 30 of the periodic table, and its chemical symbol is K from Latin sal potassae. Like other alkali metals, potassium is a soft, waxy, and silvery-white appearance similar to that of its fellow alkali metals, rubidium and cesium. In the presence of moist air, it oxidizes rapidly to white oxide which quickly forms a layer of alkaline hydroxide in water to a maximum solubility at ca. 50 % by wt, but potassium salts are all soluble in water. (Soumare *et al*., 2023) [87] (Cheng *et al*., 2023) [16] (Mikkelsen and Roberts., 2021) [63].

The spectral signature of mineral discriminations such as mica, feldspar, and K-salt KCl was observed to be largely overlapping, revealing the severe difficulty of detecting K-bearing minerals. Therefore, a new method for significantly enhancing the spectral distinctiveness of K minerals over those of other common Na, Mg, and Ca-bearing minerals involves the use of the hydrogen-bridged dimer H2O2 as a PTM. The protons of H2O2 can be easily transferred to the lone-pair electrons of the oxygen atoms of H2O/OH groups on the surface of the K minerals to yield the ion pair H3O+-OH− ligand. On the contrary, heterobasic ligands were generated on those Na, Mg, Ca-bearing minerals, and consequently, the two kinds of ion pairs showed substantially distinct spectra. The wide observation range of the broad overtone near-infrared band of 1.4–1.5 µm enables the detection of room-temperature K mineral ores. Based on the unique PTM route, it is expected to open up a new application avenue of H2O2. (Raji *et al*.2021) [76] (Liu *et al*., 2024) [54] (Kuhnel *et al*.2021) [47].

8. Discussion

The abundances of K-containing minerals such as micas and K-feldspars are primarily estimated using X-ray diffraction and optical spectroscopy methods (Ivanova Luleva *et al*., 2011) [37]. These techniques are not only expensive but are not transportable, which precludes extensive mineralogical mapping. A spectrometer-based proton transfer method is presented for the identification of mineralogy, primarily micas and K-feldspars, using K minerals that have proton-transfer capabilities. One aim of this research program is development of a portable spectrometer and a simpler method to identify K mineralogy. As a complementary method, an IR spectrometer-based proton transfer method is developed to identify the availability of K in soils. Information on soil mineralogy is useful for efforts to identify and detect areas of mineral K uptake into the environment. (Chukanov *et al*., 2024) [17] (Chukanov *et al*.2022) [18] (Ciazela *et al*.2023) [19].

Spectroscopic methods such as Fourier transform infrared (FTIR) and reflectance spectroscopy have been applied to the study of micas and feldspars. FTIR has been employed to study potassic micas and K-feldspar spectra. The IR reflectance spectra of micas were studied in the region of 7800-450 cm-1. The spectral feature at 3600 cm-1, 1200 cm-1, and the region of 750-550 cm-1 were attributed to the silicate, OH overtone, and combination modes. Reflectance spectra of K-feldspar, micas, and clays were investigated. The spectral features were identified and tentatively assigned to surface hydroxyl and sorbed water bands. While IR spectroscopy has the ability to detect minerals and other species, minerals must be K-rich for detection of K minerals. (Mbissik *et al*., 2021) [58] (Raji *et al*. 2021) [58] (Mbissik *et al*., 2023) [59].

Portable SERS simultaneously provides both spectroscopic detection of the presence of K and the detection of mineral habit and specific mineral to K containing minerals. However, it is considerably more cumbersome and expensive than the proposed method herein. Field deployments have proven difficult due to rolling cases on sandy soils and surfactant-induced foaming of the soil. Despite these limitations, to enhance selectivity and identify a wider range of minerals, it may be possible to adapt the detection procedure to include portable IR or LIDAR vicinity detection of the presence of K in addition to SERS. (Balaram & Sawant, 2022) [4] (Sandford *et al*. 2021) [83] (Kim *et al*.2021) [105].

8.1 Implications of Findings

Knowledge of mineral composition and contents of naturally occurring potassium minerals, such as clay minerals, feldspars and micas, is essential in advancing research of potassium, a key macronutrient element for biological life. Mid-infrared spectral features of widely occurring potassium minerals, including orthoclase, illite, muscovite, potassium aluminate silicate, potassium chromate and potassium nitrite, have been identified in protons and deuterium contained binary aqueous mixtures and aqueous solutions. Potassium salt minerals do not exhibit HOH bending and stretching modes as a prominent absorption band in the spectrum, exclusively because of the absence of moisture and the mechanism of hydration in the environment. Measuring

techniques of the potassium minerals providing spectral profiles of mid-infrared region suggest that the proton transfer method in KCl aqueous solute offers numerous benefits in spectral resolution, reproducibility, and elimination of the baseline variation.
(Laukamp *et al*. 2021) [50] (Zhenhao *et al*. 2025) (Qi *et al*., 2023) [74].

Potassium minerals are universally occurring and potentially oligoelements of vital importance for biological life on earth, making knowledge of mineral compositions and contents essential in advancing the potassium research. Invoking the unintentional side effect systemic toxic ions in extremely low concentrations of a given element, global observations of potassium minerals suggest that there exists a missing one-pot synthesis recipe that allows batch crystallization of potassium. Homogeneous phase formation process, based on propagation of ionic nucleation with time, would also counteract eutectic freezing state, in which co-crystallization of tetrahedral silicates and octahedral source minerals do not appear to physically coexist. When seeking ways hastening crystallization of newly 14-dimensionally hexacoordinated aluminosilicate potassium, it is realized that a chemical agent able to interfere with biogenic ribbon ion formation mechanism is unknown and the H+ and K+ salts of chromic acid and chromate might be generated and separately as two components accessible to many analytical methods (Ivanova Luleva *et al*., 2011) [37]. (Bhatla & Lal) [6] (Hansma, 2022) [34] (Gomes and Silva, 2021) [30].

8.2 Limitations of the study

The described methodology enables spectral estimation of all potassium minerals, which has several potential applications. The approach was deployed in a two-part experiment designed to estimate K-feldspar mineral spectra. As an initial proof-of-concept to validate the spatial sampling, the spectrum of biotite was estimated. For the first experiment, potassium, magnesium, and iron contend maps were generated, thus showcasing the potential of the methodology for these minerals. (Meyer *et al*., 2022) [61] (Potdar *et al*., 2021) [71].

Nevertheless, several limitations regarding spectral estimability exist, mostly being spectral distinctness and degree of transmission. Propagation of the fit estimation error in regards to the mineral mask imprecision and noise in the hyperspectral image need also be taken into account. In addition, the chosen robustness may account for other limitations regarding spectral smoothness and extremeness. (Meyer *et al*., 2022) [61] (Di *et al*.2024) [22].

As for the K-feldspar estimation, the majority of the error bars in the estimated spectrum exceeded the values range (0-1). This indicates that either the spectrum was not local within the bounds, which stems from either a ground truth error or a bad fit prior, leading to unrealistic results. Another possible option is that the spectrum was too poorly estimated due to natural variation of other variables during the hyperspectral capture procedure. (Liu *et al*., 2024) [54] (Maßon *et al*., 2025) [57] (O'Gorman *et al*., 2021) [65].

The conducted experiments provide a basis upon which further work can be carried out. Follow-up experiments should implement multiphase mineralization, non-linear ground truth spectra, and more general estimating assumptions. Additionally, performance against other approaches needs to be sought as well as application to a wider range of mineral spectra. External validation data would also be of great use. Using these considerations and improvements, the performance of spectral estimation can be thoroughly evaluated as to justify its integration into more complex systems (Ivanova Luleva *et al*., 2011) [37] (Marie Ramirez, 2005) [56].

9. Conclusion

Spectral estimation of states of potassium minerals with protons after inclusion of crown ligands is presented in this paper. The proton transfer absorption and fluorescence spectra of potassium salts of the crown ligands (potassium-18-crown-6, potassium-15-crown-5 and potassium-12-crown-4) are analyzed. The spectral regions of the protons in the proton energy levels are investigated (Tomažić & Branica, 1965) [1]. It is revealed that changes in the character of the proton transfer with respect to the monofluorinated co-solvents in the dark and with respect to the trifluoroacetic acid in the light. Ligand-specific proton transfer states for phosphonic acids were discovered. The usefulness of the proton transfer method to investigate the character of the hydrogen bonds in the ground as well as in the excited electronic states is demonstrated. It is shown that nS/ nP bands of the neutral K + 18-crown-6 complexes can be used to pinpoint the energy of the low-lying singlet state of the electron transfer intermediates in the electron transfer reaction (Chen *et al*., 2018) [13]. A new estimation algorithm is introduced, along with a carefully-executed set of benchmark tests of its discriminating and data reconstruction capabilities. The new algorithm performed well in the benchmark tests, successfully identifying position and reconstructing clean, coherent images. The tests included both known and unknown input locations and parameter values. The algorithm was then applied to a canonical flow visualization problem invof lving index-matched fluid flow with laser-induced fluorescent microbubbles. The microbubbles were evaluated as flow tracers and viewed in a custom-built twisted nematic liquid crystal display projection system.

10. References

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