



## Research paper

# Optimising rational chemical analysis for quantitative determination of the composition of clay in soils

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## ABSTRACT

A fractional (rational) chemical analytical method is proposed by which the material composition of clay rocks can be quantified and the clay-forming minerals present can be characterised. Subjecting raw clay to this procedure allows for the determination of the chemical composition of its fine-grained fraction, the amount and composition of exchangeable cations, water-soluble salts, carbonates and colloidal minerals, and the amount of amorphous silica and free quartz. A new, effective method is proposed for the qualitative and quantitative evaluation of the amorphous component in clays. This involves extracting colloids by treating the clay fractions with Tamm's reagent, a buffer solution of oxalic acid and ammonium oxalate with a pH of 3.25. Additionally, through calculations based on the results of chemical analyses, the illite content (derived from the content of non-exchangeable potassium oxide) and the chemical composition of the clay residue are determined. This enables the rock-forming clay mineral to be characterised and its structural chemical formula to be determined. This allows prediction of the physico-chemical and technological properties of the clay.

## 1. Introduction

Kaolin minerals, smectites, and illite are the most common types of clay mineral (Grim et al., 1951, 1953; Brigatti et al., 2006, 2013; Bergaya and Lagaly, 2013). Kaolin minerals are among the more finely dispersed of high-quality refractory clays. Illite is the main rock-forming clay mineral and is secondary in ball clays and fire clays. The variety of types of clay rocks and their distinct behaviour in the engineering process leads to a need for detailed research to predict and characterise their basic technological properties.

Clay rocks have a complex material composition comprising a mixture of clay and non-clay minerals. The key physico-chemical and technological properties of argillaceous rocks primarily depend on the nature and content of their clay components. Determination of the mineral type of 'the clay substance' is complicated, laborious and possible only with the use of complex modern physical and chemical methods of analysis.

The overall chemical composition of clay rock reflects the compositional peculiarities of all of its constituent minerals, both clay and non-clay; therefore, it cannot be used to determine the type of these minerals or to characterise them quantitatively. However, the individual components of the chemical composition do allow predictions to be made regarding the mineralogical composition and properties of the

rock. For example, an  $\text{Al}_2\text{O}_3$  content exceeding 30% indicates that an argillaceous rock has a predominantly kaolinite composition.  $\text{Al}_2\text{O}_3$  content in the range of 20–30% may indicate a composition dominated by illite (in the case of monomineralic clays) or a mixture of illite and kaolinite (in the case of a multimineral clay component). An  $\text{Al}_2\text{O}_3$  content below 20% is evidence that the clay is of montmorillonite type (Vakalova and Pogrebenkov, 2002; Vakalova et al., 2002). The presence of  $\text{Fe}_2\text{O}_3$  in amounts less of than 1.0% indicates white clay after calcination, from 1% to 2% imparts a yellowish shade to calcined material, and with  $\text{Fe}_2\text{O}_3$  of > 2% the palette changes from yellow (3–4%) to red (> 4%). The presence of alkali metal oxides ( $\text{Na}_2\text{O} + \text{K}_2\text{O}$ ) of up to 1.0% in the gross chemical composition of a clay where the finely dispersed component is predominantly kaolinite is a predictor that sintering will be difficult, and > 1.0% signifies good sinterability without sacrificing high fire resistance (Vakalova et al., 2009).

The development of modern physico-chemical methods of analysis (X-ray diffraction, thermal, microscopic, IR spectroscopy, etc.) has made it possible to qualify individual clay minerals of different types, even in mixtures of discrete particles or interlaminae, to a high degree of certainty (Johns et al., 1954; Worrall, 1959; Brown, 1980; Grim, 1988; Reynolds, 1992; Griffen, 1999; Hillier, 2000; Battaglia et al., 2006; Joussein et al., 2005; Petit et al., 2006; Clayton and Pearce, 2007). However, if these clay minerals belong to the same group, their

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identification becomes problematic (Kaufhold, 2006; Kaufhold et al., 2008). For the most part, concerns arise with minerals commonly found in fire clays such as kaolin and halloysite, especially if halloysite is represented by variants with different contents of chemically bound water. The most complete list of methods for diagnosing halloysite is found in the work of authors such as Sand and Brindley (Sand and Bates, 1953; Sand and Ormsby, 1954; Brindley et al., 1963; Brown, 1980; Moore and Reynolds, 1997; Joussein et al., 2005). These authors have concluded that the X-ray method is unsuitable for the analysis of mixtures of kaolinite-halloysite minerals. Sand and Bates (1953) demonstrate the presence of halloysite is masked in X-ray photograms when the kaolin content exceeds 30%. The preliminary physico-chemical treatment of clay by certain organic liquids (e.g. saturation using ethylene glycol or glycerol) extends the diagnostic capabilities of thermal analysis, as they form complexes with hydro-halloysites. The formation of these complexes forms the basis for the qualitative determination of the presence of hydrohalloysite in mixtures with halloysite and kaolinite (Sand and Ormsby, 1954; Carr and Chih, 1971; Churchman et al., 1984; Hiller and Ryan, 2002; Horvath et al., 2003; Joussein et al., 2007). The consistent position of the endothermic effect at 500–600°C on the derivatogram indicates that halloysite or kaolinite is present in the clay. The bifurcation of endothermic effect indicates that hydrohalloysite is mixed with halloysite or kaolinite or the joint presence of these minerals. Methods other than X-ray analysis have also been used to diagnose mixtures of kaolinite-halloysite minerals (Ledoux and White, 1964; Theng et al., 1984; Singh and Gilkes, 1992), but the quantitative accuracy of these methods is not yet verified.

The properties of a clay rely not only on its mineral composition but also the 'crystallinity' of the clay-forming minerals. Violations of the crystallinity of the structure vary in degree depending on the type of clay mineral. They are most characteristic of montmorillonite, and to a lesser extent, kaolinite group minerals. Some have suggested that one of the main causes of a disordered structure in clay minerals are isomorphic substitutions by ions with a different degree of oxidation. This may occur in octahedral, in the case of kaolinite (Worral, 1959; Hinckley, 1963; Khalissi and Worral, 1982) or tetrahedral sheets (Grim, 1968), or in both at the same time, as is most typical for montmorillonite (Christidis, 2008). The result is a weakening of the hydrogen bonds between the tetrahedral and octahedral sheets. Differences of opinion on the nature of isomorphic replacements in disordered kaolinites (octahedral and/or tetrahedral sheets) can be explained by flaws in previous studies of the chemical and mineralogical composition of clays (Vakalova, 1997a, b).

In addition to the nature of clay minerals and the degree of perfection of their crystal structures, the properties of clay rocks are affected by the presence of amorphous material. Almost every clay contains organic and inorganic amorphous components (Biermans and Baert, 1977; Meier and Menegatti, 1997; Menegatti et al., 1999). Silica, hydrous oxides of iron and manganese, iron sulfide, etc., occur in the form of gels in the natural silicate raw material (Lagaly and Dekany, 2013; Nakato et al., 2015). For example, Vakalova (1997a, b) provided evidence of the formation of colloidal shells around clay particles. This may result either from the isolation of the gelatinous breakdown products of the parent rock during formation of the clay or the dissociation and dissolution of the surface layer of the clay particle by water. These gels have a chemical composition close to that of the clay mineral. They are capable of gelation or gel-formation even at the relatively high water content that results from the formation of the skeleton-base by clay particles coupling at their less hydrophilic ends. Another reason for the formation of gels is the adsorption of colloidal particles onto the surfaces of the crystallised clay minerals. The presence of a sufficiently large amount of an amorphised constituent in a clay rock affects its plastic properties and pyrochemical activity (the ability to form a mechanically strong structure of components resulting from reactions in the solid state at a heat-treatment below the sintering temperature, 600–700°C).

Currently available methods for the quantitative determination of soil colloids are notably imprecise (Chakraborty, 1978). Many publications are devoted to studies of the composition and properties of clay rocks, soils and soil minerals. Because soils and clays are natural substances composed of different minerals, a wide variety of methods are required to analyse these objects, and these are constantly being improved and perfected. The CBD method (the citrate bicarbonate dithionite method) has been proposed as an effective method for removing colloidal and free iron oxides from a soil (Jackson, 1958) but it is not recommended for clay studies since it involves the partial destruction of clay minerals with an alkaline reagent. The current article makes the novel proposal of using Tamm's reagent to extract colloids from clays, as it does not destroy clay minerals.

Of particular significance for determining the mineralogy of clay raw material is the analysis of the composition of fine-grained fractions (< 5 µm) of clays. These fractions are usually polymineralic, including, along with the clay minerals, admixtures of minerals and substances such as quartz, opal, cristobalite, compounds of iron, carbonates and organic matter. The complexity and inaccuracy of quantitative determination of the clay minerals and trace constituents in clay rocks and their fine fractions by known physical and chemical methods necessitate additional work to develop better alternative approaches.

This paper proposes a complex fractional (rational) chemical analysis method that achieves more accurate determination of the phase-component and type of clay-forming minerals in clay rocks than is possible with pre-existing physico-chemical methods. This includes the determination of the general (total) chemical composition and the use of various chemical approaches (e.g. treatment with water, acid and soda) to extract all or characteristic parts of individual minerals from the clay.

## 2. Research methods

The method presented herein for determining the material composition of clay rocks was tested on > 60 samples of clay. This article details the work on the most representative thirty-two of these, which have different chemical compositions and particle size distributions (Fig. 1).

The proposed method investigates the chemical and physical composition of these clays by way of their fine fractions, which are < 5 µm in equivalent spherical diameter and are isolated by sedimentation. The aggregated clay structure was broken down through trituration into a plastic dough state over one hour, followed by transfer to a slurry state with a density appropriate for analysis in the clay range using the pipette method. The required clay fraction was isolated by elutriation (in accordance with Stokes' law, by the extraction of clay slurry at a certain depth and a certain time during the sedimentation of the clay particles in pH 6.7 distilled water without dispersing and coagulating additives).

The chemical composition of the fine-grained fraction was determined by traditional silicate chemical analysis (Easton, 1972) (Table 1). The gross chemical compositions of the fine-grained fraction (clay minerals) of clay loam in molecular form are characterised by the following coefficient change boundaries:

(0.037–0.120) R<sub>2</sub>O (0.212–0.540) RO R<sub>2</sub>O<sub>3</sub> (2.56–3.64) SiO<sub>2</sub> (1.0–1.65) H<sub>2</sub>O<sup>+</sup> (1.73–2.88) H<sub>2</sub>O<sup>-</sup>.

Quantitative determination of the material composition of the clays was carried out by rational chemical analysis using a procedure that has been successfully employed by the authors in numerous studies. This procedure uses direct analyses to determine the chemical composition of fine-grained fraction (< 5 µm), the amount and composition of the exchangeable cations, water-soluble salts, carbonates and the amorphised constituent (colloids), and the amount of amorphous silica and free silica (Fig. 2).

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