#### ARTICLE



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## Trace Elemental Profiles of School Chalk from Few Companies in Punjab (India) by WDXRF Technique

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## A B S T R A C T

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Received: 7 June 2016 Accepted: 1 July 2016 Published: 20 July 2016 Chalk powders from different companies in Punjab (India) were analyzed using WDXRF technique. The studies focussed on the quantitative analysis of elements in school chalk to ensure the safety of its use. The elements like calcium, aluminium, iron, silicon and chromium were detected from the low Z region and Ba, Sr, Pb, Zr from the high Z region. Presence of these elements in significant concentrations in school chalk confirmed that it is an irritant and occupational hazard. It is suggested to use protective equipments like filtered mask for mouth, nose and chalk holders. This study also suggested the use of advanced mode of techniques like digital boards, marker boards and power point presentations to mitigate the occupational hazard for classroom chalk.

# **KEYWORDS**

Trace elements, School chalk, Punjab, WDXRF technique.

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## INTRODUCTION

Chalk board teaching is a conventional method of teaching from prehistoric times. Chalkboard is mandatory for a conventional classroom. The use of the school chalks poses health hazards to a teacher. As the chalk is scrapped on the chalk board the particles are released into the surrounding air. The emanated chalk dust from board may settle on the floor as well as dispersed out into surrounding based on the ventilation of classroom. Inhabitants (teachers and students) inhale fraction of school chalk dust, which usually becomes trapped in the mucous layer of the throat and upper lung. The inhabitants with healthy respiratory system can expel the dust through cough and remaining material will be absorbed to respiratory organs. For the inhabitants with chronic breathing issue like asthma, an exposure to chalk dust can aggregate the problem further. The dust settled on the body parts, clothes and furniture etc. may lead to skin irritations and allergies. Chalks (dusty or dustless) are commonly made up of limestone (CaCO<sub>3</sub>) or gypsum (dehydrated form of CaSO<sub>4</sub>) as their main constituent. Kaolinite (hydrated aluminium silicate), carboxymethylcellulose (CMC), poly vinyl alcohol, starch is present in small quantities. It may also contain some impurities like silica and

coloured chalks contain some metals [1]. The traditional method of manufacturing school chalks is to make clay like paste with calcium carbonate and allow it cure in a chalk shaped boards. To overcome the chalk dust related health risks, manufacturers started producing dustless chalks. Instead of forming chalk crayons through individual moulds the new chalk mixture is extruded into ropes, then cut to sizes and allowed into dry. These dustless chalks are also generating the dust particles but the particle size is much heavier and tends to fall directly on the floor instead of floating in the air [2]. Exposure to air borne chalk dust has been reduced but the accumulation of chalk dust elsewhere is problematic. Low concentration of metals in chalk dust can be analyzed by the application of WDXRF [3]. The present study deals with the elemental analysis of unused school chalk using WDXRF technique.

## EXPERIMENTAL

Chalk samples of different companies were collected from the different cities of Punjab (India) *viz*. Nawanshahr, Chandigarh, Phagwara, Jalandhar and Hoshiarpur.

Chalk samples were initially ground with a mortar and pestle and then pressed into pellets of 23 mm diameter with pressure of 40 kN m<sup>-2</sup>. WDXRF was carried out to study their elemental characteristics.

**WDXRF:** The elemental analysis of Chalk samples was carried out using using a Bruker S8-Tiger WD-XRF technique. The WDXRF set up consisted of a Rh anticathode X-ray tube as source of excitation, four analyzing crystals (XS-55, PET, LIF200, LIF220), a flow proportional counter (for light elements) and a scintillation counter (for heavy elements). Analyses were performed under helium atmosphere to avoid powder loss in the analytical chamber, which may occur under vacuum conditions.

The system offers the most flexible and compact beam path. In combination with the high performance X-ray tube and advanced analyzer crystals, this compact beam path gives highest intensity and analytical speed. The calibration functions have been selected out of the calibrations implemented by the software of X-ray spectrometer S4 («SPECTRAPLUS», 2002). The S8 TIGER can analyze all elements from beryllium to uranium in a wide variety of sample types. The total time-to result was 113 s, including loading, evacuation, analysis and reporting of the results. The peak acquisition time was optimized using the built-in SpectraPlus® software interface, which calculates the time necessary to achieve an average selected detection limit. The acquisition time varies, therefore, among elements as well as among concentrations of a given element (*i.e.*, the lower the concentration, the greater the time). To avoid any excessively long acquisition times, a maximum time was set for each element, which varies from 30 to 100 s. The background measurement times have been fixed manually, generally at 10 s, except for a few trace elements. The overall measurement time is about 40 min per sample (i.e., 36 samples/ 24 h). The higher resolution of WDXRF provides advantages in reduced spectral overlaps, so that complex samples can be more accurately characterized. In addition, with high resolution backgrounds are reduced, providing improved detection limits and sensitivity.

## **RESULTS AND DISCUSSION**

Fig. 1a and 1b shows a typical X-ray spectrum of a chalk from different cities of Punjab.

Spectra plus software automatically determined the elemental concentration in chalk samples using Lachance-Traill formula;

$$\mathbf{m}_{i} = \mathbf{A}_{0} + \mathbf{A}_{1}\mathbf{I} \times \left(1 + \sum_{j \neq i} \alpha_{ij} \cdot \mathbf{m}_{j}\right)$$

where  $m_i$  is the element concentration and I the measured intensity of the corresponding line and  $m_j$  are the concentrations of the other elements j.  $A_0$  and  $A_1$  are the coefficients of the calibration regression line, respectively offset and slope. They are stored either in the Line library if a default calibration is used or in the calibration file if a specific calibration is used.  $\alpha_{ij}$  are the interelement matrix coefficients. They can be calculated theoretically based on fundamental physical values like absorption coefficients and secondary fluorescence enhancement. This is a simplified model of the physical reality.

It is seen from Table-1 that there is significant amount of low Z elements like Ca, O, Si, Al, Fe, Mg, K, Cl, Na, Ti while the elements like Ba, V, Zr, Sr, Zn, Rb, Cr, Cu, Ni, Ga were present in lesser quantity. Only one sample which is slate has Pb as its element. The exposure to excess concentration of calcium dust can be a physical irritant to eyes, nose, mucous membranes and skin of humans. Calcium is in the range of 23-27 %. Contact of calcium carbonate causes redness, pain and inflammation of the eyelids [4]. The silicon concentrations of settled chalk dust samples are noticed in the range of 20-30 %. The silicon is used for binding purpose so this may be the reason for the higher concentration of silicon in chalk samples. The excessive exposure to silica causes the bronchitis, emphysema and pneumonia [4]. The concentration of sulphur is also high in some chalk samples such as Kamal chalk and are in the range of 15-19 %. Iron was observed with higher concentration in many samples. The exposure to iron shows symptoms like metallic taste, fever and chills, chest tightness and cough [4]. The aluminium, nickel and chromium concentrations were also noticed in higher concentration in some samples. The excessive exposure to nickel and chromium causes skin irritation and allergies like contact dermatitis, eczema, conjunctivitis [5].

Corraza et al. [5] studied the effect of concentration of some elements e.g., nickel, cobalt, etc. and compounds like calcium carbonate, calcium sulphate, carboxymethylcellulose etc. present in different commercially available blackboard chalks. The cause of periorbital dermatitis among college lecturer or teachers are contact allergy, irritant contact dermatitis and atopic dermatitis. Metals found in the powder of blackboard chalk are the main cause of airborne allergic contact dermatitis. They concluded that the nickel elicitation threshold on healthy skin in adults was 5-10 ppm and a concentration of 0.5 ppm has been found to be sufficient to trigger contact dermatitis on irritated skin. For cobalt, the minimum elicitation concentration was approximately 2 ppm. The good manufacturing practice to keep the level of nickel and cobalt as lower than 5 ppm and risk of sensitization was further reduced if it was lowered than 1 ppm.

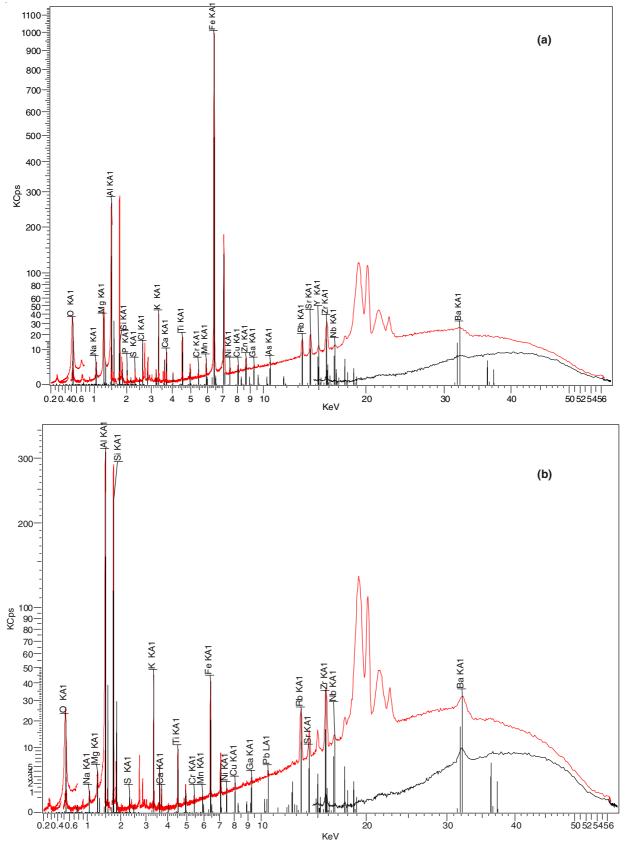


Fig. 1. (a) & (b) X-ray spectrum of two different chalk sample from WDXRF

Olusegun *et al.* [6] assess the concentrations of heavy metals in ready-to-eat foods offered for sale in some major towns of South-West Nigeria using graphite-furnace atomic absorption spectrophotometer. The results show that the lead concentration in ready to eat food and fried ready to eat food were ranged between 3.8 to 23.6 mg/100 g of sample (38 to 236 ppm) and 6.9 to 23.6 mg/100 g of sample (69 to 236 ppm), respectively. Chromium concentrations were found between

TABLE-1 CONCENTRATION OF ELEMENTS PRESENT IN CHALK POWDERS (ppm)									
Chalk	Elements								
	0	Si	Al	Fe	Mg	K	Cl	Na	Ti
Multanvi mitti	394900	247000	89200	88400	31600	21200	10100	7100	6800
Kamal chalk (pink)	469200	29000	8800	5400	12600	2400	800	1500	600
Kamal chalk (blue)	463900	32500	10600	4400	_	2300	300	1300	800
Chand tara slate	354100	318000	107200	5500	2100	37200	88	1900	5700
Kores dustless	458900	6700	1900	2400	4000	1100	200	-	200
Himanshu chalk	440100	4100	1100	800	1300	400	400	400	-
Jain chalk (yellow)	460700	27600	8800	4400	5000	2300	1900	2000	700
Chalk	Elements								
	Ca	Ba	V	Zr	Sr	Zn	Rb	Cr	Cu
Multanvi mitti	4200	400	200	200	200	200	200	77	74
Kamal chalk (pink)	241500	-	-	100	5600	-	-	-	93
Kamal chalk (blue)	238800	-	-	58	-	23	-	-	26
Chand tara slate	900	700	-	200	100	-	300	100	43
Kores dustless	265500	-	_	5	900	22	6	_	18
Himanshu chalk	271400	-	-	6	1900	-	-	-	-
Jain chalk (yellow)	243400	_	-	90	5400	_	-	-	30
Chalk	Elements								
	Ni	Ga	S	Mn	Р	Nb	Y	As	Pb
Multanvi mitti	72	22	1000	500	500	20	16	14	
Kamal chalk (pink)	25	_	151700	200	200	_	-	_	_
Kamal chalk (blue)	-	-	171000	-	200	-	-	-	-
Chand tara slate	19	27	200	_	200	20	_	_	48
Kores dustless	-	-	193700	100	85	-	-	-	-
Himanshu chalk	-	-	-	196000	-	-	-	-	-
Jain chalk (yellow)	20	_	170000	100	100	-	_	-	_

2.1 to 38.5 mg/100 g (21 to 385 ppm) of sample which approaches acute toxicity values. They concluded that the consumption of these read to eat foods which contains higher concentration of heavy like lead, chromium, cadmium etc. results in health hazards. Satsangi et al. [7] estimated the effect on human health from indoor concentration of fine and inhalable particles and its associated toxic metals. Trace elements like Cd, Co, Cr, Cu, Fe, Mn, Pb, Sb and Zn in particulate matter were reported by ICP-AES technique. in silico Study confirmed the higher cancer risk assessment by Ni as compared to other carcinogenic metals e.g., Cr, Cd etc. They concluded that the Ni actively formed coordination complex with histone protein of Human tissue and its impact on epigenetic changes cause lung and nasal cancer. In our study, the concentrations of nickel found in some blackboard chalks were much higher than the threshold for contact dermatitis and airborne dermatitis. The levels of nickel were 72, 25 and 19 ppm for Multanvi mitti, Kamal chalk (pink) and Chand tara slate, respectively. The rest of the samples reported a very much lower concentration for nickel, which can't be even detected by WDXRF technique. However the chromium concentrations were reported only in Multanvi mitti and Chand tara slate as 77 and 100 ppm, respectively. The present study doesn't find any traces of cadmium element in all the samples underwent WDXRF analysis.

### Conclusion

The results of this study confirmed the presence of the elements like Ca, Al, Fe, Si, Ni and Cr are in significant concentrations. The exposure to elements like Ca, Al, Si, Fe, Ni and Cr causes irritation to eyes and skin, cough, potential health symptoms includes accumulation to lungs. The study confirmed that black board chalk is an irritant and occupational hazard. It is suggested that the people working in chalk dust areas are suggested to take some protective measures [8] like using filtered mask, chalk holders and proper ventilating conditions. The advanced methods like marker boards, power point presentations and digital boards can reduce the impact on occupation health of classroom chalk user and WDXRF is an ideal technique for trace elemental analysis of chalk powders. To know the level of toxicity it is important to know the oxidation states of the elements presently detected. Hence it is planned to carry out a synchrotron study to obtain the oxidation states of the elements present.

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