Accurate determination of six common fillers in fine papers, newsprint, and recycled stock by X-ray fluorescence spectrometry

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ABSTRACT: The method allows for accurate and reproducible determination of fillers such as kaolinite, calcium carbonate, titanium dioxide, talc, muscovite and sodium aluminosilicate levels in commercial fine papers, newsprint, decorative papers, coated offsets, and headbox furnish. The filler levels are derived individually from the elemental analysis and their exact concentrations are established according to stoichiometric conditions calculated and verified by a small software program. The method is independent of interfering factors, such as basis weight, thickness and filler distribution in the z-direction of the paper sheet, and is adaptable to most X-ray fluorescence spectrometers available in analytical or testing laboratories.

KEYWORDS: Fillers, paper grades, recycling, spectrometers, test methods, x ray fluorescence, x ray spectroscopy

In the present environment of recycled stock, high filler levels (up to 30%), frequent evaluation of offset and writing papers, super-calendered (SC)-filler-loaded newsprint and other "exotic" grades, a rapid and precise X-ray method capable of simultaneous determination of six common paper fillers is desirable. X-ray methods used for the characterization and quantification of individual fillers in paper were described by Garey and Swanson *(1)*, Parham and Hultman *(2)*, Thomas and Heithur *(3)*, and Bluhm, Jones, and Deslandes *(4)*. These contributions described the use of X-ray diffraction (XRD) for identification and quantification of filler levels in paper. The use of X-ray fluorescence analysis (XRF) was recommended for more precise quantification of fillers in paper. The latter (XRF) method is presently used in mills for on-line or off-line monitoring of clay (kaolinite), calcium carbonate, and titanium dioxide. Kaolinite, calcium carbonate, titanium dioxide, talc, muscovite, and sodium aluminosilicate, known as "hydrex", are commonly used fillers. These were the object of our interest as a quick laboratory test for various grades of commercial fine papers and newsprint as well as handsheets and machine furnish samples. The disadvantages of X-ray diffraction methods for quantitative determination of fillers of paper are due to limitations, such as time consuming scans and poor quantification of fillers, caused mainly by variable crystallinity, particle size distribution, and "preferred orientation" of the fillers in the sheet. The X-ray diffraction methods can detect only fillers or compounds which have a crystallographic lattice. This restriction would outright eliminate quantification of calcined clay and sodium aluminosilicate (hydrex), both of which have an amorphous, non-crystalline structure. Because of this limitation, the use of X-ray diffraction is restricted to filler or mineral phase identification, especially in situations where different modifications are present (i.e., anatase and rutile, TiO_2, or calcite and aragonite, $CaCO_3$), or in those cases where "exotic" fillers, such as gypsum, barium sulfate, zeolite, etc., are present in the sheet. XRF spectrometry offers rapid, precise, and repeatable results with a high degree of accuracy through

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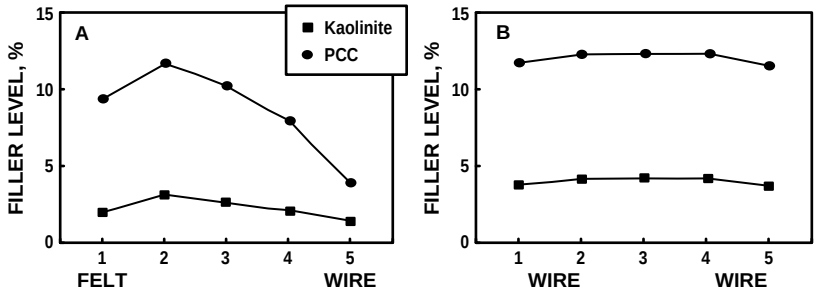
stable calibration procedures. Calibrations, once properly established, hold for a long time (usually for several years) and small day-to-day variations in slope and intercepts of the calibration lines are adjusted by measurement of one or two synthetic (glass) monitor samples. To some extent, X-ray fluorescence results are also affected by absorption, "matrix effects" (effect of other fillers), the physical distribution of the filler on the fiber and in the sheet (*z*-direction), basis weight, and purity of the individual fillers. The objective of this work was to eliminate or minimize these effects and develop a suitable method based on XRF for the precise quantitative evaluation of filler levels in any paper or furnish.

Disadvantages of existing filler determination methods

Most of the existing methods used to determine fillers by X-ray fluorescence (XRF) require that the paper be in a sheet form. This is a great advantage in production, where the X-ray source and a detector are mounted directly on the paper machine. Other commercial paper filler testers are usually based on radioisotope sources and require only a small piece of paper sheet for filler determination. The accuracy and precision of these instruments depends strongly on basis weight, paper thickness and, most of all, on the filler distribution in the *z*-direction of the paper. When a certain grade of paper is produced on a given paper machine, the first two parameters (basis weight and thickness) are readily available, and the third one (filler distribution in *z*-direction) is fixed by the configuration and geometry of the forming section (single or twin wire). One can usually recognize two basic *z*-direction filler distributions in papers, asymmetric *(5)* for single wire (**Fig. 1A**) and roughly symmetric for twin-wire machines (**Fig 1B**).

1. Filler profiles in the *z*-direction of the paper sheet. A: single wire machine. B: twin wire machine.



I. Percent oxide and corresponding filler level ranges in calibration standards

Filler	*Element as % oxide*	*Calibration range, % oxide*	*Std. devn., %*	*% Range filler in paper*
	SiO_2	0 - 18	0.02	-
Kaolinite	Al_2O_3	0 - 16	0.04	0 - 30
Titanium dioxide	TiO_2	0 - 32	0.02	0 - 32
Calcium carbonate	CaO	0 - 14	0.02	0 - 25
Talc	MgO	0 - 2	0.02	0 - 6
Muscovite	K_2O	0 - 2	0.03	0 - 20
Hydrex	Na_2O	0 - 2	0.03	0 - 20

It is obvious that the important *z*-direction distribution of the filler is an unknown variable in most paper grades that come to the laboratory for filler level testing. When paper sheets are presented to the XRF filler tester, it can matter on which side of the sheet (wire of felt) the measurement is made. Paper sheets made on a single wire machine show XRF intensities of the light elements (such as Na, Si, Al, K and Ca) differing by as much as ± 30% on either side of the sheet. This effect is due to the limited depth from which the X-rays of light elements are generated, and to different filler loads on each side of the sheet. The anomaly is called "two-sidedness" of the sheet. For sheets produced on a twin wire machine, filler distributions in the *z*-direction are more symmetrical, and the intensity differences are smaller.

As the X-ray elemental peak intensities are related to the individual filler levels, the "two sidedness" of the sheet results in large calculated filler level errors if based only on determination of the two sides. In the 1960s and '70s, the filler levels averaged approximately 6–10% of the sheet weight. Filler loadings doubled in the past decade to 15–25% in some grades and the errors generated by the two-sidedness of the sheet became intolerable and difficult to correct.

Pulverized pellet method

One way to eliminate, or to drastically minimize the intensity errors caused by thickness, basis weight, and filler profile is to pulverize the sheet with good mixing and press it into a pellet. Such pulverization will make paper powder more homogeneous and eliminate most of the sheet-related errors. This method is

II. Conversion factors and stoichiometric relations used in the calculation of filler levels in paper

Oxide	*Conv. factor*	*Filler*	*Formula*	*F. W.*[a]
% Al_2O_3	x 2.53 =	% Kaolinite	$2SiO_2.Al_2O_3.H_2O$	258.17
% TiO_2	x 1.00 =	% Anatase or rutile	TiO_2	79.90
% CaO	x 1.79 =	% Calcium carbonate	$CaCO_3$	100.09
% MgO	x 3.14 =	% Talc	$Mg_3Si_4O_{10}(OH)_2$	379.34
% K_2O	x 10.81 =	% Muscovite	$KAl_3Si_3O_{10}(OH)_2$	398.32
% Na_2O	x 10.50 =	% Hydrex	$Na_2O.Al_2O_3.4SiO_2.4H_2O$	476.36

% Talc x 0.634 =	% SiO_2
% Muscovite x 0.494 =	% SiO_2
% Muscovite x 0.310 =	% Al_2O3
% Hydrex x 0.685 =	% SiO_2
% Hydrex x 0.129 =	% Al_2O_3
% Hydrex x 0.019 =	% MgO

Ratio of $Al_2O_3/2SiO_2$ in kaolinite is	1/1.17
Ratio of $3MgO/4SiO_2$ in talc is	1/1.99
Ratio of Al_2O_3/SiO_2 in muscovite is	1/1.73[b]
Ratio of Al_2O_3/SiO_2 in hydrex is	1/5.30[b]

[a] F.W. = formula weight
[b] ratios determined from several XRF analyses

currently used in our laboratory and is described in this work.

Experimental

After numerous attempts to pulverize paper in the most efficient way, we have decided to use dry pulverization in a laboratory type blender. Approximately 4–5 g of paper (usually half of an 8 1/2- x 11-in. sheet) is cut into approximately 1/2- by 1/2-in. pieces or passed through a small office paper shredder. The pieces are loaded into a Waring laboratory blender *(6)* and pulverized for 1–2 min at the low speed setting. The sharp rotating blades cut and pulverized most papers or newsprint quickly into a fluff or "snow" with 70% of particle size close to 300 µ (50-mesh). After use the glass jar of the blender is conveniently cleaned by a strong vacuum and wiped with a tissue paper. The pulverization is usually short (1–2 min), but quite effective in breaking down and mixing the sample. The short pulverization time prevents separation of the fibers and filler, which could result during prolonged paper grinding. Other types of grinding equipment were tried, but resulted either in filler/fiber separation or difficulties with cleaning. Often water and organic solvents had to be used between charges to avoid cross-contamination of samples.

Preparation of the pellet

Approximately 4 g of the prepared paper "fluff" is pressed at 25-ton ram load into a 32-mm diameter XRF sample die using a small hydraulic press. An aluminum backing cup (Spex or Chemplex type) is used for better dimensional stability and support. The resulting 4-mm thick pellet must be flat with a very smooth surface. Excessive surface roughness can cause errors in the measurement of the intensities. The use of binders added to the paper powder for better "packing" and pressing is not required and generally not recommended. The high pressure and a short pause of 10 s at the maximum pressure (before release) is sufficient to produce a hard, durable and flat pellet.

Intensity measurement

A Philips PW-1400 wavelength dispersive spectrometer, equipped with six crystals (LiF 200 and 220, PET, Ge, In-Sb and PX-1-Ovonyx) was used for the actual determinations. Sample holders with copper masks are used to eliminate the presence of aluminum or titanium in the sample holder material. The sample is rotated during the peak intensity measurement in order to minimize surface and particle size effects. The

III. Computer output of the results as printed by the 'FILLERS' program

Fillers in paper by x-ray fluorescence method SMX-32

Sample No.1: D-STI-Offset			400°C Ash = 17.90	R-SiO_2 = 0.17		R-Al_2O_3 = 0.00
% TiO_2	*% CaO*	*% K_2O*	*% SiO_2*	*% Al_2O_3*	*% MgO*	*% Na_2O*
0.06	5.47	0.00	3.35	2.53	0.10	0.13
% Kaolin	*% TiO_2*	*% $CaCO_3$*	*% Talc*	*% Muscovite*	*% Hydrex*	*% Sum*
6.40	0.06	9.79	0.31	0.00	0.00	16.87
Sample No. 2: R-REC-Bond			400°C Ash = 28.46	R-SiO_2 = 0.13		R-Al_2O_3 = 0.00
% TiO_2	*% CaO*	*% K_2O*	*% SiO_2*	*% Al_2O_3*	*% MgO*	*% Na_2O*
1.09	9.43	0.03	4.32	2.86	0.39	0.07
% Kaolin	*% TiO_2*	*% $CaCO_3$*	*% Talc*	*% Muscovite*	*% Hydrex*	*% Sum*
6.98	1.09	16.88	1.22	0.32	0.00	26.70
Sample No. 3: V-SCA-News			400°C Ash = 30.20	R-SiO_2 = 0.15		R-Al_2O_3 = 0.00
% TiO_2	*% CaO*	*% K_2O*	*% SiO_2*	*% Al_2O_3*	*% MgO*	*% Na_2O*
0.44	0.13	0.03	13.99	11.60	0.07	0.00
% Kaolin	*% TiO_2*	*% $CaCO_3$*	*% Talc*	*% Muscovite*	*% Hydrex*	*% Sum*
29.09	0.44	0.23	0.22	0.32	0.00	30.46
Sample No. 4: R-SCA News			400°C Ash = 30.20	R-SiO_2 = 1.24		R-Al_2O_3 = 0.00
% TiO_2	*% CaO*	*% K_2O*	*% SiO_2*	*% Al_2O_3*	*%MgO*	*% Na_2O*
0.03	0.03	0.68	14.37	10.01	0.20	0.32
% Kaolin	*% TiO_2*	*% $CaCO_3$*	*% Talc*	*% Muscovite*	*% Hydrex*	*% Sum*
19.56	0.03	0.05	0.63	7.35	0.00	29.18
Sample No. 5: C-SCB-News			400°C Ash = 0.20	R-SiO_2 = 0.07		R-Al_2O_3 = 0.00
% TiO_2	*% CaO*	*% K_2O*	*% SiO_2*	*% Al_2O_3*	*% MgO*	*% Na_2O*
0.00	0.09	0.00	0.07	0.00	0.00	0.18
% Kaolin	*% TiO_2*	*% $CaCO_3$*	*% Talc*	*% Muscovite*	*% Hydrex*	*% Sum*
0.00	0.00	0.16	0.00	0.00	0.00	0.41

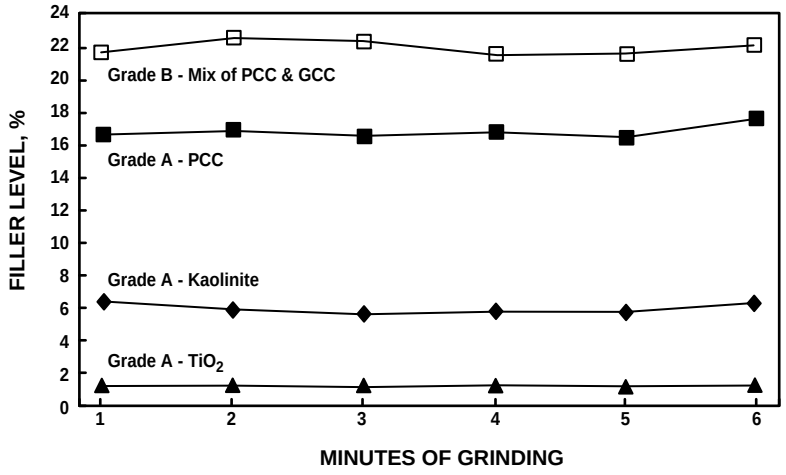
Note: % sum include also: %R –SiO_2 + %R – Al_2O_3 + %Na_2O R = residuals after stoich. calculations

total measurement time per sample was 4 min, and this time also included time lost due to automatic changing from sample to sample.

Calibrations

Since international paper filler standards or "Certified Reference Materials" of filler levels in paper were not commercially available, in-house prepared standards were used. Several commercial alkaline or acidic fine papers, SC newsprint, and handsheets made with variable filler levels were used as standards. The exact concentrations of fillers in these standards were established indirectly by ashing of the paper and fusing the ash with lithium tetraborate. The fused discs were analyzed against a calibration supported by 24 international certified reference silicates and silicate rocks originating from Britain, France, South Africa, and the United States. A total of 30 in-house standards or reference materials were prepared, out of which 26 were selected for the final calibrations. The elemental concentrations of the calibration standards and the analyzed samples are expressed as weight percent oxide in the same fashion as for any other mineral or silicate sample. This notation makes the stoichiometric and filler level calculations simpler. It may be important to note that the concentration distribution of the individual fillers in a set of calibration standards should be kept close to random in order to eliminate bias. Dilution of high filler paper with pure

2. Effect of grinding times on filler losses in two (90 g/m^2) fine paper grades



IV. Statistical reproducibility of filler levels obtained on six independent samples from one lot of fine paper. Grinding time 2 min

	TiO_2	*Kaolinite*	*PCC*	*Talc*
	1.06	5.79	16.88	1.32
	1.07	5.82	17.11	1.38
	1.03	5.39	16.49	1.19
	1.07	5.97	17.08	1.35
	1.02	5.34	16.43	1.16
	1.03	5.51	16.56	1.29
Average =	1.05	5.64	16.76	1.28
Std. devn. =	0.02	0.23	0.27	0.08

commercial cellulose or pulp is not recommended, due to possible introduction of concentration patterns into the calibration set. The calibration ranges of the prepared reference standards are shown in **Table I**.

For practical reasons and expedience, the method was set up for the determination of only six different fillers. This number can be increased to eight if one expects to analyze papers containing barium sulfate or some other exotic fillers such as alumina trihydrate, $Al(OH)_3$, or zeolites.

Linear regressions and inter-element corrections

The intensities of the individual elements were determined using K-alpha peaks. Intensities of silicon, aluminum, magnesium, and sodium peaks were corrected for background. The linear regressions used for the calibrations incorporated the Lachance-Trail *(7)* inter-element matrix correction model modified by DeJongh *(8)* with coefficients precalculated by an off-line software. These were in the form:

$$C_i = (D_i + E_i R_i)[1 + (\Sigma \alpha_{ij} C_j/100)] \quad (1)$$

where

C_i = concentration of element i

D_i = intercept of the calibration line

E_i = slope of the calibration line

R_i = countrate ratio for element

α_{ij} = precalculated alpha coefficients for element i

C_j = concentrations of other elements in the specimen.

It is also possible to use other correction algorithms or derive the correction coefficients by regressions on the calibration standards only. The latter, however, can often lead to incorrect signs or magnitudes and calculate coefficients valid only within the calibration ranges.

Filler concentrations

Two basic assumptions have to be made when considering quantitative determination of fillers based on elemental analysis. The purity of the filler used (at least 95% pure) and its chemical stoichiometry (corresponding closely to the chemical formula). We found that these assumptions hold true for most fillers used in North America and Europe. Iron is present in talcs and clays as a minor impurity (up to 4% Fe_2O_3) and some sulfur is found (at 3.5–4% SO_3) in various sodium alumino silicate (hydrex) production batches. The purity of calcium carbonate and titanium dioxide used in the paper industry is usually higher than 98%, the exception being ground calcium carbonate (GCC), which may contain some quartz (0.5–1%), dolomite, and iron. These impurities, if present at low levels, would only marginally affect (decrease) the calculated concentration of a filler. For the pulp as a medium, we assume that the mineral impurities (pulp ash value) do

not exceed 0.6% of the total dry weight. This is true for most properly washed, unbleached, or bleached pulps. Elements such as Ca, Ti, K, and Mg are "selective" or primary elements on which the initial filler concentrations of calcium carbonate, titanium dioxide, muscovite, and talc are respectively based. Sodium, aluminum, and silicon are secondary elements used for calculations of sodium aluminosilicate (hydrex) and kaolinite (clay) content. Once the initial levels of filler are established, the software calculates back and subtracts the individual oxide concentrations generated by the stoichiometry. Residual percentages of unused SiO_2 or Al_2O_3 are printed to indicate stoichiometric anomalies. The objective is to balance and match the individual oxide levels for all the fillers present in the sample. The sum of all fillers determined in a paper sample could be matched or constrained to an ash value determined at 400°C, if necessary. The lower temperature used for paper ashing (400°) prevents partial decomposition of kaolinite or calcium carbonate at temperatures above 500°C. In general, the sum of the individual fillers calculated by the software will be slightly lower than the ash value, due to the impurities present in the fillers and the background elements in the pulp. This difference usually does not exceed 2–3% relative on the total sum. Large differences between the sum of the fillers and the 400°C ash almost always indicate the presence of "exotic" filler or mineral impurities containing elements not determined by the analysis. Some of the stoichiometric relations used to calculate and verify the filler content from the analyzed elemental concentrations are shown in **Table II**.

Results

Results calculated by a small software program "FILLERS" written for the personal computer are shown in **Table III**. The input into the program is a peak intensity file created by the XRF spectrometer or manual input of the results from the keyboard. The second option is used when elemental concentrations are obtained by other analytical methods such as atomic absorption or plasma spectroscopy (AA, ICP).

The statistical reproducibility of results for a recycled grade with multiple filler levels is shown in **Table IV**. Most of the errors on reproducibility or "repeatability" of results originate from the actual inhomogeneity of the paper sheet. Errors caused by filler loss during disintegration of the sheet affect the results only marginally even when prolonged grinding times are used. **Figure 2**, obtained on two different fine papers grades, illustrates this quite clearly.

Conclusions

The X-ray fluorescence method using pulverized samples pressed into a disc is more precise than filler determination methods reported previously. The pulp filler heterogeneity (in *z*-direction) and its effect on filler level determination has been eliminated completely by the use of the novel paper grinding technique. The resulting average errors in the determined filler levels are in the order of 1–3% relative. The accuracy of the obtained results would be mainly dependent on the quality of the prepared calibration standards. The method was successfully used on hundreds of samples analyzed at the Research Centre during the past four years. It was instrumental in the product grade development, benchmarking, troubleshooting, and calibration of on-line machine sensors in the mills. The method was also used in the filler evaluations at the headbox level, coated stock formulations, etc. ■

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