

Sodium / Potassium Ratio and Hygroscopicity of Civil War Era Black Powder

K. L. and B. J. Kosanke

Several years ago a sample of Black Powder, which had previously been recovered from US Civil War era cannon balls (ca. 1865), was made available for analysis. This made possible a brief comparative study of the Civil War era sample and one representing currently produced Black Powder. That study found the performance of the Civil War era powder sample to be roughly comparable to current production Black Powder.^[1] Following that initial study, a very brief study was conducted regarding the purity of the potassium nitrate used in the Civil War era powder sample. Specifically, the molar percentage of sodium to potassium was determined, and those results were compared with the results from two more recently produced powders. This was of interest because it was speculated that the potassium nitrate in the Civil War era Black Powder might have been of lower purity with regard to the amount of sodium present (potentially as sodium nitrate). If that were the case, it might contribute to the susceptibility of the powder to absorb moisture, potentially leading to its degraded performance under battle field conditions.

The samples for analysis were prepared by the prolonged agitation of small portions of Black Powder in hot (near boiling) water, followed by filtration and washing of the residue with additional amounts of hot water. (Note that this method may have also extracted some components of the ash in the charcoal. However this is thought to be of relatively little consequence.)

The resulting aqueous solutions were then analyzed spectrally to determine the ratio of sodium to potassium, using their emissions at approximately 589 and 768 nm, respectively. (For analysis, the samples were aspirated into a gas flame to produce the emissions, which were then analyzed using an Ocean Optics CHEM2000 spectrometer.) For calibration, a 0.1 molar standard solution with a sodium to potassium mole ratio of 5.0% was used. Table 1 presents the results of the analyses.

Before discussing these results, a note of caution is appropriate. Only one sample of the Civil War era and Dupont powders were available for analysis, where it would have been preferable to have analyzed multiple representative samples of each powder type. Further, while it is not thought to have produced any interference, it would have been preferred that the standard solution contained somewhat less sodium. Nonetheless, for the samples analyzed, it seems clear that the relative amount of sodium in Black Powder has increased substantially over the years. The Dupont powder (ca. 1950) was found to have approximately 4 times the amount of sodium found in the Civil War era powder sample; and the Goex powder was found to have approximately 12 times the amount of sodium. Accordingly, the supposition that the sample of Civil War era Black Powder might have been made using potassium nitrate with a higher concentration of sodium than current production powder

Table 1. Sodium to Potassium Ratios for Solutions Prepared from Black Powder Samples.

Source	Approximate Date of Mfg.	Peak Ratio (Na / K)	Mole Percent (Na to K)	Relative Amount
Calibration Std.	—	0.189	5.0	—
Civil War	1865	0.0056	0.15	≈ 1.0
Dupont	1950	0.024	0.63	4.2
Goex	1995	0.067	1.80	12.

was definitely not found to be correct. Somewhat surprisingly, the more modern powders contain substantially more sodium.

The relatively high sodium to potassium ratio found in the solutions prepared from the Black Powder samples does not necessarily correspond to a high susceptibility to problems with moisture absorption. Accordingly, it was decided to proceed with determination of the moisture absorbing tendency (hygroscopicity) of the three different era powder samples. This was accomplished by first reducing the size of the powder grains with a mortar and pestle to approximately 100 mesh. This was done to eliminate any differences from the powder samples being of different granulations. However, it also reduced the length of time taken for the powder samples to reach their equilibrium moisture contents, after being placed in various constant humidity environments (hygrostats). Following particle size reduction, the samples (each a little over 3 grams) were dried for 4 hours at a temperature of 110 °C. (Note that this temperature was more extreme than the conditions for drying used in moisture determination according to the current military specification.^[2] The reason for using the higher temperature was simply to be assured of the complete dryness of the samples before testing.)

The constant humidity chamber used in this study was a large glass desiccator with the desiccant removed and a tray containing one of a series of saturated aqueous solutions installed in its place. Depending on the nature of the saturated solution (and the temperature in the lab, 17 °C) various constant humidity levels were produced.^[3,4] Using saturated solutions of lithium chloride, potassium carbonate, ammonium nitrate, sodium chloride, strontium nitrate, and barium chloride, relative humidity levels of 11, 43, 67, 76, 88 and 92 percent were produced in the test chamber. In each case the time of exposure was approximately two days, which is about twice as long as it took for the samples to come to equilibrium. (In each case, this was confirmed by continuing exposures until no further moisture was acquired by the samples). All three samples were placed in the humidity chamber at the same time, and their exposure was begun using the solution producing the lowest relative humidity level. Following exposure at one humidity level, the samples were removed, covered

and weighed. Then the tray of saturated solution was replaced with the one producing the next higher relative humidity level. (As a point of reference, note that the humidity level sufficient to cause moisture to collect on pure potassium nitrate, at the temperature of the lab, is 95%, a little higher than the maximum relative humidity used in these measurements.)

Table 2 lists the percentage weight gain for each of the three samples for each relative humidity exposure level, and these values are presented graphically in Figure 1. As suspected, the current production Black Powder (Goex), with the greatest sodium content, experienced the greatest weight gain upon exposure to humidity (i.e., it was the most hygroscopic). However, based on its lower sodium content in comparison to the Dupont powder, it had been anticipated that the Civil War era powder would be the least hygroscopic. Instead it was found that the Civil War era and Dupont powders both gained about the same amount of weight (moisture), with the Dupont powder gaining slightly less.

Table 2. Percentage Weight Gain for Samples of Black Powder as a Function of Relative Humidity Exposure.

Relative Humidity (%)	Weight Gain (%)		
	Civil War	Dupont	Goex
11	0.36	0.22	0.46
43	0.84	0.75	1.01
67	1.13	1.03	1.41
75	1.25	1.15	1.68
88	1.46	1.31	2.66
92	2.00	1.78	3.73

Since the results of the hygroscopicity measurements for the Civil War era and Dupont Black Powders were somewhat unexpected, perhaps it worth speculating as to the reason. It is thought that the results (percentage weight gains) are correct for two reasons: 1) for each of the humidity exposures, the Dupont powder always gained less than the Civil War era powder, and 2) the initial weights were confirmed by re-drying the powder samples after the highest humidity exposure. This leaves the sodium to potassium ratio measurements potentially suspect. While it would have been appropriate to redo

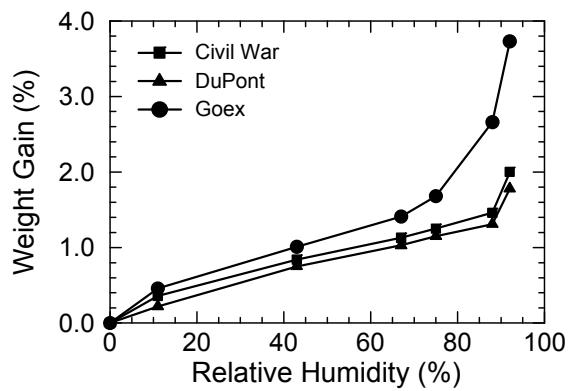


Figure 1. Percent mass gained as a result of exposure to various relative humidity levels.

these determinations, that was not done for four reasons: 1) the necessary instrument was in the process of being reconfigured and would not be available for some time, 2) interest in this project relative to other ongoing projects had diminished substantially, 3) it is possible that the sodium to potassium results are fully correct (see below), and 4) the answer to the question initially being raised was already in hand (see below).

First consider the possibility that the sodium to potassium ratios were indeed correct. It would seem possible that the relatively higher sodium content of the Dupont powder (compared with the Civil War powder) was in a form that was successfully extracted after the prolonged agitation in hot (near boiling) water, but which was mostly non-hygroscopic, even at the highest relative humidity exposure used in these tests. One example of how that might occur, could be that much of the sodium in the Dupont powder was bound in some non-hygroscopic form, possibly associated with the charcoal in the powder.

Next consider the initial supposition, regarding whether battle field humidity was likely to have been especially detrimental to the performance of the Black Powder being used during the Civil War. Based on the weight gain measurements of the sample tested, this would clearly seem not to have been the case, since the current production powder was found to be the most hygroscopic. The fact that the Dupont powder apparently was slightly less hygroscopic than the Civil War era powder tested is interesting but not particularly relevant to the question initially posed.

Acknowledgements

The authors are grateful to F. Ryan for previously supplying the sample of Civil War era Black Powder used in this study and to L. Weinman for commenting on a draft of this article.

References

- 1) K. L. & B. J. Kosanke and F. Ryan, "Performance Study of Civil War Vintage Black Powder", *Journal of Pyrotechnics*, No. 9, 1999; also in *Selected Pyrotechnic Publications of K. L. and B. J. Kosanke, Part 5(1998 through 2000)*, Journal of Pyrotechnics, 2002.
- 2) *Military Specification: Powder, Black*, MIL-P-223B, 1962.
- 3) *Standard Practice for Maintaining Constant Relative Humidity by Means of Aqueous Solutions*, American Society for Testing and Materials, E-104-85, 1991.
- 4) *CRC Handbook of Chemistry and Physics*, CRC Press, 1995, p 15-25.