A Chemical Education Article-

Statistical comparison of results of redox titrations using $K_2Cr_2O_7$ and KIO_3 in the undergraduate analytical chemistry lab

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ABSTRACT

*Reducing the quantity of hazardous substances used and hazardous waste generated by undergraduate laboratory experiments is important. However, simply replacing hazardous compounds with less hazardous reagents may not retain the pedagogical (or analytical) goal of the experiment if the chemistry does not fundamentally work. We evaluated several literature-based replacement oxidants for $K_2Cr_2O_7$ (potassium dichromate) and identified KIO_3 (potassium iodate) as the only chemically viable alternative for thiosulfate standardizations, consistent with use of iodate by others. Using ANOVA analysis, two years of student results where $K_2Cr_2O_7$ was used as the oxidant were compared with two years of student results where KIO_3 was used as the oxidant (ANOVA p-value for precision = 0.684; ANOVA p-value for accuracy = 0.638). This **comparison** of multiple years of student data enabled us to confidently eliminate toxic Cr(VI) from a quantitative iodometric titration in our second year analytical chemistry laboratory, while students maintained a high level of both accuracy and precision.*

Keywords: Green Chemistry, Analytical Chemistry Education, Safety / Hazards, Titration / Volumetric Analysis.
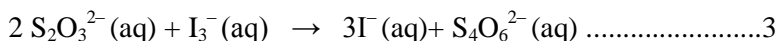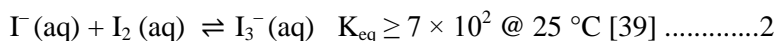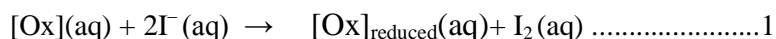
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INTRODUCTION

Redox titrations remain important components of an analytical chemistry laboratory curriculum, because this relatively straightforward method gives high-precision results with experimentally-determined uncertainty in the 4th digit. Such attainable precision facilitates the development of a common student learning objective for analytical chemistry: producing results that are both precise and accurate[1]. Potassium dichromate ($K_2Cr_2O_7$) is a common oxidant in redox titrations due to many desirable characteristics as a primary standard: stable to oven drying and storage in ambient conditions; widely availability; solubility in water; relatively low cost; and high molecular weight. However, the dichromate anion contains Cr(VI) (hexavalent chromium) which is carcinogenic, toxic, and genotoxic.[2-5] Historically, the "chemical convenience" of this chemical outweighed concerns about its hazardous

nature. The green chemistry principles that have emerged in the last two decades attempted to find chemically viable processes with a reduced environmental impact.[6-7] As we educate future chemists, it seems obligatory to consider these principles as we design laboratory activities for our students. In the past 20 years, in chemical education much green chemistry attention has focused on organic chemistry with a move towards less noxious solvents, reagents, and microscale synthesis.[8-12] While organic chemistry has received considerable attention,[13-17] other courses in the chemistry curriculum can also benefit from application of the 12 green chemistry principles,[18-23] including analytical chemistry.[24-25] Asakai, *et al* [26] showed that KIO_3 could replace $K_2Cr_2O_7$ in redox titrations and evaluated other oxidants, as well.[27] Given this and that IO_3^- is documented in textbooks and lab manuals available on the web.[28-33] we have not "discovered" that KIO_3 is a useful redox primary standard in educational settings.   Rather, this report ***compares*** the accuracy and precision of iodometric titrations using $K_2Cr_2O_7$ as a primary oxidant for two years with iodometric titrations using KIO_3 as a primary standard for two years when used by second or third year chemistry and biochemistry students.

MATERIALS AND METHODS

Chemical Methodology
Standardization of Thiosulfate: The general approach of thiosulfate / iodometric titrations is outlined in analytical chemistry textbooks.[34-35] Eq. 1 shows that when a known quantity of primary oxidant [Ox], classically $K_2Cr_2O_7$, reacts with an excess of iodide (from KI) in acidic solution (pH ~0.5) to generate iodine (I_2) stoichiometrically. Eq.2 shows that in the presence of excess iodide (I^-), triiodide (I_3^-) was thermodynamically favored.[36-37]   Finally, Eq.3 shows triiodide reacting with the student-prepared sodium thiosulfate ($Na_2S_2O_3$) solution to be standardized. The oxidant was the limiting reagent (reactant) and was stoichiometrically related to thiosulfate.[38]

$$[Ox](aq) + 2I^- (aq) \; \rightarrow \quad [Ox]_{reduced}(aq) + I_2 (aq) \;.......................1$$

$$I^- (aq) + I_2 (aq) \; \rightleftharpoons I_3^- (aq) \quad K_{eq} \geq 7 \times 10^2 \; @ \; 25 \; °C \; [39] \;.............2$$

$$2 \, S_2O_3^{2-} (aq) + I_3^- (aq) \; \rightarrow \quad 3I^- (aq) + S_4O_6^{2-} (aq) \;.......................3$$

Oven-dried (150°C for $\geq$ 90 min), analytically-massed quantities (~100s of mg) of oxidant were added to a 250 or 500 mL Erlenmeyer flask and dissolved in 25-50 mL of distilled or deionized water. A second solution contained a stoichiometric excess of KI dissolved in 25-50 mL of distilled water and ~1-2 mL of 6 M HCl. The oxidant and KI solutions were mixed immediately before beginning the titration and I_2 (or I_3^-) forms rapidly, which was titrated with the student's thiosulfate solution. The titration was performed relatively quickly because atmospheric oxygen can react with excess iodide in acid to form I_2 (or I_3^-), which would interfere with the analysis. Citrate, added when the oxidant was $K_2Cr_2O_7$, complexed with Cr^{3+} which further drives the set of titration reactions to the right. Starch indicator was added before the end point was reached, but only after the I_2 (or I_3^-) concentration has been significantly diminished and the solution lightens to light reddish-brown. The titration end point goes from blue to colorless. Ten students used approx. 9 grams of toxic $K_2Cr_2O_7$ and produced ~15 liters of ~5mM Cr(III), which were managed in a costly, separate waste stream.

Precisely reaching the end point of the titration when using $K_2Cr_2O_7$ was complicated by the fact that the Cr(III) citrate complex ion was light blue in color which was somewhat difficult to distinguish from a low concentration starch , iodine solution.   In contrast, iodate was colorless in both oxidized and reduced states. For highly precise work it was not possible to prepare a stock solution of I_2 (or I_3^-), rather, the stoichiometric quantity of iodine was prepared immediately before each titration.[40]
Chemicals and Equipment: Reagents were used as supplied by a variety of typical academic chemical vendors. Students prepared solutions in standard volumetric glassware with pre-boiled deionized or

distilled water. 1-2% (w/v) starch indicator solution was prepared using standard methods. Throughout the course, students used 50 mL burettes that they calibrate.[41]

Statistical comparison of titration data: In the pilot survey, one thiosulfate solution was prepared and standardized using different candidate replacement oxidants. Results of repeated titrations ($N = 3$ or 5) for potential replacement oxidants were compared pair-wise with titrations using $K_2Cr_2O_7$ ($N = 5$), where Student's t-test compared the concentration
while the F-test compared the variance.[42-43]

The multi-year deployment study utilized student-reported data for four years (four class sections), total $N = 38$. For two years, students performed iodometric titrations using $K_2Cr_2O_7$ as the oxidant; for two subsequent years, students performed titrations using KIO_3 as the oxidant. Precision (relative uncertainty) between the two sets of students was compared using the coefficient of variance in PPT (parts per thousand) units, COV_{PPT} ($\equiv 1000 \cdot s/\langle x \rangle$), where s is the standard deviation of the data set and $\langle x \rangle$ the average. Accuracy was compared by comparing both the signed and unsigned difference between the student-reported and the accepted %Co in the compound ($\Delta\%Co = \%Co_{reported} - \%Co_{true}$). These metrics were compared using the p-value from a one-way ANOVA analysis performed in Excel. Consistent with standard practice, ANOVA p-values ≤ 0.05 indicated that the difference between the groups was NOT due to random chance; that was, for small ANOVA p- values, the null hypothesis, there was no difference between groups, was rejected. If, on the other hand, the ANOVA p-value was > 0.05, it was not disproved that there was a difference between groups (or more colloquially stated in the positive, there was no difference between groups).

RESULTS AND DISCUSSION

Approach and goal: Our objective in this project was to find a less noxious substance, both from a personal health and environmental perspective, which second and third year chemistry and biochemistry students could use to obtain results of equal (or better) precision and accuracy, while altering a minimal number of experimental procedures. The specific goal was to identify and to validate *in student hands* one viable replacement, not to prepare an exhaustive list of every possible replacement. Specifically, we tested whether using the more benign oxidant IO_3^- instead of the toxic oxidant $Cr_2O_7^{2-}$ gave a GROUP OF STUDENTS statistically-similar high-levels of accuracy and precision in their chemical analyses: the standardization of a thiosulfate solution which was then applied to the problem of %Co determination. While IO_3^- appears an adopted oxidant in educational settings,[28-33] we are unaware of any peer-reviewed **_comparison_** between $Cr_2O_7^{2-}$ with IO_3^- in the literature, particularly in the context of highly precise and accurate results by a group of analytical chemistry students.

Pilot survey: Potential replacements were identified by reviewing analytical chemistry texts,[35] which were confirmed to be unlisted by the US EPA (Environmental Protection Agency). Potential replacements were also assessed for personal risk using Baker Saf-T-Data values that attempt to quantify Health, Contact, and Reactivity personal safety hazards. These are analogous to the analogous NFPA codes commonly included on MSDSs where 4 represented the highest risk. Finally, we considered the economic impact by considering pricing on the bases of price per gram and price per gram per oxidizing equivalent (normalized to dichromate). Table 1 summarizes the information considered when selecting potential replacement primary oxidants.

Table 1. Attributes of various replacement oxidants discussed in the text. Personal safety is from Baker Saf-T-Data; Chemistry performance and procedural complexity summarize the results of this study. Pricing information is based on 500g quantity at $\geq$ 99.0% purity from a common US supplier; prices in parenthesis are price per gram per oxidizing equivalent relative to $K_2Cr_2O_7$.

	Environment (EPA) Listed	Personal safety			Procedural Complexity	Pricing
		Health	Contact	Reactivity		$/gram
$K_2Cr_2O_7$	Yes	4	4	3	Med	$ 0.46 $ (0.46)
KIO_3	No	2	1	3	Low	$ 0.73 $ (0.53)
KBrO3	No	2	2	3	Low	$ 0.20 $ (0.11)
Cu	No	3	1	2	High	$ 0.37 $ (0.08)

In the pilot survey, 1 L solution of $Na_2S_2O_3$ solution was prepared and then standardized within 1-2 days using the oxidants listed in table 1. Pair-wise t-tests and F-tests revealed that only KIO_3 and $K_2Cr_2O_7$ gave statistically equivalent results at the 95% confidence level in regards to **both** $[S_2O_3^{2-}]$ (t_{calc}= 1.67 < $t_{crit,95\%}$ = 2.31) and the standard deviation (F_{calc} = 1.21 < $F_{crit,95\%,4/4}$ = 6.39). Accordingly KIO_3 was selected for the $F_{crit,95\%}$ deployment study for students to replace $K_2Cr_2O_7$ in thiosulfate standardization titrations.

Deployment study results: Student data (masses and volumes) were retained for each valid[44] thiosulfate titration performed for two years using $K_2Cr_2O_7$ and for two years using KIO_3. To reduce the risk of error in the analysis due to using different atomic masses, or other calculational inconsistencies, $[S_2O_3^{2-}]$ and %Co values were re-calculated.

Thiosulfate Standardization (Comparison of Precision): Since each student prepared their own thiosulfate solution, the students' precision of $[S_2O_3^{2-}]$ was analyzed, but their accuracy was not considered. Students' precision was compared using COV_{PPT} based on $\geq$ 3 replicate titrations. As a control for precision where nothing was changed, COV_{PPT} was also compared for standardization of student-prepared solutions of both HCl and NaOH (COV_{PPT} for NaOH ANOVA p=0.508; COV_{PPT} for HCl ANOVA p=0.414). These statistics for COV_{PPT} of [NaOH] and [HCl] from the two groups were interpreted as an internal control to indicate the level of variation between sections since these procedures were entirely independent of oxidant. The first rows of table 2 summarize and compare some statistical metrics for the precision-linked COV_{PPT} metric for determining $[S_2O_3^{2-}]$. The large ANOVA p-value $\gg$0.05 indicate that was no presumption for the hypothesis that there was a difference in the precision correlated with switching oxidants, which might be more succinctly stated in the positive as 'the precision appears to be independent of oxidant'. As the right-hand columns of the table further indicate, the population distribution at various levels of precision was very similar between the two oxidants.

Table 2. Comparison of Precision. The avg and stdev are those for COV_{PPT} $(=1000 \cdot s/\langle x \rangle)$ from the indicated population. The population distribution columns indicate the total number of students (out of N) that met the indicated precision standards, e.g., "$n<8$" is the number of students who obtained results with $COV_{PPT} \leq 8$ppt.

		COV_{PPT}				Population distribution			
	N	avg	stdev	med'n	range	$n<8$	$n<15$	$n<20$	ANOVA p
Expt: $[S_2O_3^{2-}]$ COV_{PPT}									
Years Using $Cr_2O_7^{2-}$	19	22.8	20.2	17.9	63.9	6	9	10	
Years Using IO_3^-	19	26.2	29.7	16.4	101.9	6	9	11	**0.684**
Expt: %Co COV_{PPT}									
Years Using $Cr_2O_7^{2-}$	19	39.6	41.1	27.9	172.9	5	6	14	
Years Using IO_3^-	19	46.7	51.5	41.0	212.5	4	7	13	**0.638**

APPLICATIONS

Determination of Cobalt in a transition metal complex
Comparison of precision : As part of a multi-week lab project in our quantitative analysis course, second and third year undergraduate chemistry and biochemistry students determined the mass percent of Co (%Co) in a coordination compound of unknown (to the student) stoichiometry by performing an iodometric redox titration using thiosulfate that they standardized as described above. In the reaction scheme above, generalized Eq 1 is replaced with specific Eq.4.

$$2 \text{ Co}^{3+}(aq) + 2 \text{ I}^-(aq) \rightarrow 2 \text{ Co}^{2+}(aq) + I_2(aq) \text{ -------- } 4$$
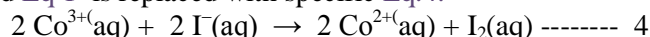
Specifically, in the procedure used, the cobalt in the sample was oxidized to Co(III) by treatment with 6% aqueous H_2O_2. Co(III) oxidized excess I– ultimately to I_3^- (Eq 4), Eq 2) which was then reduced to iodide by titration with the students' standardized thiosulfate solutions delivered from student-calibrated burettes to the starch endpoint (from inky blue to colorless). The procedure to determine %Co was independent of the oxidant used to standardize thiosulfate, but the value of %Co depended on the accuracy of students' $(S_2O_3^{2-})$. The thiosulfate, standardized with either $K_2Cr_2O_7$ or KIO_3, was used to determine the %Co for which both the precision (COV_{PPT}) and accuracy were analyzed. The lower rows in **table 2** compare the precision achieved between the two groups of students. Again, the large ANOVA p-value was inconsistent with a difference in COV_{PPT} for %Co when either iodate or dichromate was used to standardize the thiosulfate solution, as was the case for COV_{PPT} in $(S_2O_3{}^{2-})$.

Comparison of Accuracy: Unlike the students' thiosulfate solution concentrations, it ***was*** possible to compare the accuracy of results for the %Co determination for which an accepted value of %Co was known (by the instructor and based on the chemical formula). Table 3 summarizes and compares results for Δ%Co $(=\%Co_{reported} - \%Co_{true})$. Unlike the unsigned COV_{PPT}, student-determined values of accuracy were either above or below the true value; therefore, the difference (Δ%Co) was either positive or negative. The first rows of Table 3 present the analysis of absolute value of the accuracy as (Δ%Co); while the second set of rows summarizes the analysis of the ± signed data. As when comparing precision, the relatively large ANOVA p-values ($\gg$ 0.05) were consistent with there the accuracy being the same when thiosulfate solutions were standardized using different oxidants. This was true for both absolute differences and signed differences. There was what might be considered a 'sizable' numerical

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difference in the averages of Δ%Co, when the oxidants differ. However, while the ANOVA *p*-value in were slightly lower than for the precision, they remain inconsistent with the hypothesis that the Δ%Co was different (i.e., the %Co was the same). The exceptionally large range in Δ%Co for IO_3- results from one student's results. The right-hand columns in table 3. Comparison of accuracy in measurement of Δ%Co ($=\%Co_{reported} - \%Co_{true}$) determined with iodometric titration as dependent upon oxidant. $\%Co_{true}$ is the value based on the chemical formula. The population distribution columns show the number of students that were within the indicated accuracy: e.g., n<|0.5%| value of 3 means that there were three students whose accuracy was within 0.5% of the true %Co value (from 0.5% low to 0.5% high).Table 3 indicate that median and population distributions of Δ%Co were numerically similar when either oxidant was used. In summary, the accuracy of the chemical analysis was equivalent regardless of the oxidant used to standardize the thiosulfate.

Table 3. Comparison of accuracy in measurement of Δ%Co ($=\%Co_{reported} - \%Co_{true}$) determined with iodometric titration as dependent upon oxidant. $\%Co_{true}$ is the value based on the chemical formula. The population distribution columns show the number of students that were within the indicated accuracy: e.g., n<|0.5%| value of 3 means that there were three students whose accuracy was within 0.5% of the true %Co value (from 0.5% low to 0.5% high).

	N	Δ%Co metrics in percent units				Population distribution			
		avg	stdev	med'n	range	*n* < |0.5%|	*n* < |1.0%|	*n* <|2.5%|	ANOVA *p*
Expt: Δ%Co, Abs. Value: $\lvert \%Co_{rept} - \%Co_{true} \rvert$									
Years Using $Cr_2O_7^{2-}$	19	1.58%	1.93%	1.24%	9.1%	2	8	17	**0.203**
Years Using IO_3^-	19	9.66%	27.1%	1.74%	119%	3	8	12	
Expt: Δ%Co, Signed: $\left(\%Co_{rept} - \%Co_{true} \right)$									
Years Using $Cr_2O_7^{2-}$	19	0.28%	2.5%	0.89%	11.4%	2	8	17	**0.214**
Years Using IO_3^-	19	8.31%	27.5%	0.92%	125%	3	8	12	

Incorporating Green Chemistry into Chemical Education: The *comparisons* presented above demonstrated that switching away from toxic dichromate to iodate would enable college students to maintain high levels of accuracy and precision in iodometric titrations. Accordingly, we encourage other chemical educators to consider this as they develop and modify the laboratory portion of their courses. Further, as anecdotally referenced above, iodate has already achieved at some level of use in the chemical education community for certain redox titrations. In cases where instructors use or adopted iodate in favor of dichromate, student learning should be broadened to include green chemistry explicitly by guiding students to personally evaluate green chemistry principles and then applying those to a selection of reagents for use in a reaction. Specifically, when we switched oxidant from dichromate to iodate during the deployment study, students were simply informed that the experimental procedure changed from using a toxic chemical. Beyond our specific case, the web resources above[28-33] seem to make no comment about *why* iodate was selected for use. Remaining silent on the reason certain chemicals were used (or rejected), seems unlikely to invoke critical student thought as to why certain reagents were selected. Accordingly, we developed an activity for future students to enumerate the 12 principles of green chemistry, to write a short statement on their overarching goal, and to then apply them to the problem of selecting an oxidant for use in an iodometric titration. Finally, we note that analytical chemistry textbooks might consider adding environmental and personal safety to the list of desirable traits for a primary standard.

CONCLUSIONS

We have shown, by comparing multiple years of student data that in a college analytical chemistry lab where high-precision and high-accuracy results are key student learning objectives, quantitative analytical iodometric titrations can be viably performed by students replacing the more hazardous classical primary standard, $K_2Cr_2O_7$, with a greener primary standard oxidant KIO_3.   Certainly we did not 'discover' that KIO_3 can be used as an oxidant for analytical chemistry experiments, but we are unaware of a peer-reviewed COMPARISON where the same chemical analysis was performed at reasonably high levels of accuracy and precision by students with the two different oxidants.

ACKNOWLEDGEMENTS

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[38] Triiodide has the additional advantage of being water soluble, whereas the solubility of I_2(aq) lower. There is some discrepancy in the precise numerical value of K, which appears to show strong dependence on ionic strength. However all the literature reviewed gave a Keq > 600 for this reaction.

[39] There is risk of an interference effect from atmospheric oxygen: it is possible for some (small amount of) I^- to be oxidized directly to I_2 by atmospheric oxygen rather than the oxidant acting as the primary standard. This would be extra iodine would make the concentration of thiosulfate appear higher than it actually is. The rate of air oxidation is sufficiently slow that it does not affect the result if titration is complete within < 10 minutes. Accordingly, for students to obtain highly precise and accurate results it is important to work quickly and to minimize transfers of the iodine(triiodide)-containing solution to avoid mixing in oxygen.

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