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S117

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Determination of the percentage of iron in iron samples

**Introduction:**

Determination of the percentage Fe in a sample can be broken down into a series of steps culminating with a titration (1).In this lab, Fe3+ will be converted to Fe2+ using SnCl42- and a sulfuric acid-phosphoric acid reagent will be added. Excess of Sn2+ will be removed with HgCl42-. This series of steps ensures that all of the iron in the sample will be titrated. Finally, the titration of the Fe2+ with Cr2O72- yields Fe3+ and Cr3+ to allow us to determine the percent iron of the original sample. Statistical techniques of standard deviation, percent error, and uncertainty of the average of our data will allow us to quantitatively assess its quantitative accuracy and precision.

**Questions:**

Why is dephenylbenzidine as an indicator instead of simply watching for the color change of dichromate to chromic ions?

How is the graph of vs. Volume of solution similar to the titration diagram of –log[H+] vs. Volume?

What makes Cr2O72- a good oxidizing agent?

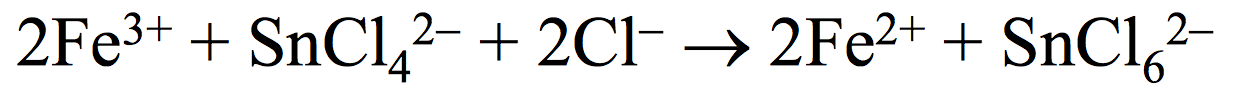
**Procedure:**

2.95 g K2Cr2O7was weighed using a mass balance and transferred to be dried in an oven at 110C for one hour. (This part was completed prior to the beginning of the lab for the second and third week). It was cooled for 30 minutes in a desiccator. It was weighed and reweighed in a glass cylinder. A bit of distilled water was added to dissolve it, and it was transferred with a glass funnel & stirring rod to a 500-mL volumetric flask. Distilled water was added to bring it to the calibration mark. The stopper was placed and it was mixed. The concentration was calculated, and it was labeled with our names. This was done for two more volumetric flasks (to prepare for the other two trials).

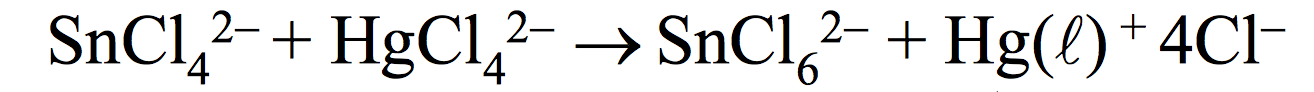
2-2.5 g of an iron-containing sample was transferred to a weighing bottle. (For this experiment, 2.4516 g was measured out). It was dried in the oven at 100C for one hour. The sample was divided and weighed into three 500-mL Erlenmeyer flasks with .25 g of the sample in each. (For this experiment, the exact amount of the iron-containing sample varied, but it is shown below in the Results section. It was recommended to use different amounts rather than just .25 g for all the trials. To measure them out, a cylinder was weighed, the sample added, and the difference between the two was used.). 10 mL distilled water and 10 mL HCl was added, and it was mixed over the burner in the hood to dissolve it. .5 M SnCl2 was added drop by drop until the yellow disappeared. 1 or 2 more drops were added to ensure all the Fe3+ reacted. The solution was let to cool down to 25C by immersing the flask in a water bath. 10 mL Hg2Cl2 was added. If the white precipitate was observed, 150 mL distillated water was added after 2-3 minutes. If gray or black solid material was observed, it was discarded. That indicated the presence of liquid mercury.

10 mL H2SO4-H3PO4 reagent (to alter the indication point by reacting with, and therefore lowering, the Fe3+ concentration) and 8 drops barium diphenylamine sulfonate (used as indicator for a color change to violet at the endpoint) were added. For our experiment, we used 12 drops of it instead of 8 for trial #3 because we hypothesized that 8 drops was too dilute after one of our trials failed to change to violet. (That trial changed to a dark green followed by black.) Before the titration, the K2Cr2O7 was loaded into the burette until the initial volume was 0 mL. (For the first trial, it was actually at 1 mL, but this was accounted for in the calculation shown below). It was titrated in the volumetric flask with .0167M K2Cr2O7 to the endpoint color violet. The final volume of the K2Cr2O7 was recorded. The difference between the initial and final volume was found, which would be the K2Cr2O7 required to titrate the iron. This was repeated until three successful trials were obtained. The percent iron was calculated from the volumes of K2Cr2O7solution used (the steps are shown in the Results section).

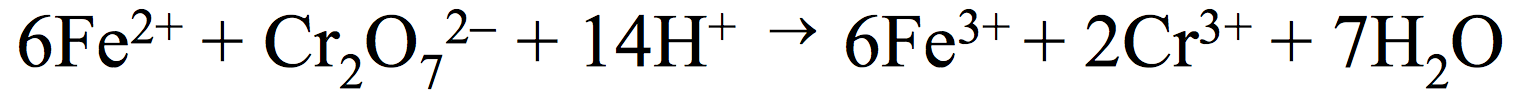
The first reaction of Fe3+ and SnCl42- in the presence of Cl- to Fe2+ and SnCl62- is shown in this reaction. The iron is reduced from 3+ to 2+ by gaining an electron from SnCl42-, which is oxidized to SnCl62- , in the presence of Cl-. Fe3+ is the oxidizing agent and SnCl42- is the reducing agent.



The excess SnCl42- is removed by oxidizing it to SnCl62- with HgCl42-.



Finally, the Fe2+ is titrated with Cr2O72- to yield Fe3+ and Cr3+. (The theory behind the redox reaction of the titration is discussed in the Discussion section).

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**Results:**

**Fig 1: Precision of each lab equipment** (6) is shown in this table. The uncertainty will be carried through for the claculations in order to determine the uncertainty for the final percentages of iron.

|  |  |
| --- | --- |
| **Lab equipment** | **Precision** |
| Mass balance | ±.0001 g |
| Volumetric flask | ±.0002 L |
| Buret | ±.00002 L |

**Fig 2: Calculation of mass samples:** The mass of the sample was calculated by weighing the glass cylinder with the sample of iron. The initial mass is the cylinder with the iron, the final mass is the cylinder without iron (except for the first trial). For the first trial, we incorrectly added 2.9454 g of the sample, so we removed the sample until the difference was enough to use for the titration. The sample mass is the difference between the two.

|  |  |  |
| --- | --- | --- |
| **Cylinder initial mass (g)** | **Cylinder final mass (g)** | **Sample mass (g)** |
| 2.9454 | 2.4954 | 0.4500 |
| 0.3376 | 0.0172 | 0.3204 |
| 0.3799 \* | 0.01200\* | 0.3679\* |
| 0.3084 | 0. 01800 | 0.2904 |

**Fig 3: Titration results**: The trials are shown in the order in which they were performed. After the third trial failed to change to violet (since it changed to green, then black), the fourth trial was performed with 12 barium drops, rather than 8.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Trial** | **Sample mass (g)** ±1.414x10-4 g | **Initial volume K2Cr2O7 (mL)** | **Final volume K2Cr2O7 (mL)** | **Vol K2Cr2O7 used in titration (mL)** | **% Fe in sample** |
| 1 | .4500 | 1.0 | 37.60 | 36.60 | 54.4% |
| 2 | .3204 | 0.0 | 26.45 | 26.45 | 55.0% |
| N/A | .3679\* | 0.0\* | Rejected\* | Rejected\* | Rejected\* |
| 3 | .2904 | 0.0 | 23.82 | 23.82 | 54.6% |

\*The third trial shown was rejected due to the incorrect concentration of SnCl2 added due to lab stockroom mistakes.

**Fig 4: Average, percent error and standard deviation:** Our average and standard deviation shown give a 2.43% error, showing reasonably good accuracy.

Our sample # 256 has the actual value 53.40% Fe.

|  |  |  |
| --- | --- | --- |
| **% Fe** | **Avg (**x̄) | **Std Dev ()** |
| 54.4% | 54.7% | 0.306 |
| 55.0% |  |  |
| 54.6% |  |  |

Percent error

% error = =

**Fig. 5: Error Propagation and Analysis for individual trials**: Error by each calculation for each trial. The calculations and corresponding variables for the errors (s with subscript) are shown below. These are the errors for the moles of dichromate used, mass of iron titrated, and percent iron in sample. The Error propagation for other measurements are below.

|  |  |  |  |
| --- | --- | --- | --- |
| **Trial** | **st (mol)** | **sf (g)** | **sp** |
| 1 | 1.118x10-5 | .00375 | .01150 % |
| 2 | 1.341x10-5 | .00449 | .00141 % |
| 3 | 1.437x10-5 | .00481 | .00167 % |

**Calculations:**

Mass of K2Cr2O7 = (Mass of cylinder + K2Cr2O7) – (Mass of cylinder) = 2.9613 g – 0.0159 g = 2.9454 g K2Cr2O7

**Sample calculation of % Fe in a sample:**

Trial 1

.03660 L K2Cr2O7 = .24561 g Fe

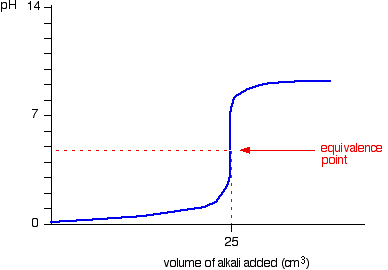
.24561 g Fe / .4500 g sample = 54.4% Fe

**Error Propagation:**

* Moles K2Cr2O7 in flask = m = (2.9454 g )=.01012 mol K2Cr2O7
* Volume K2Cr2O7 in flask =.5 L
* Mass of K2Cr2O7 errorsk2= (.0001)2 + (.0001)2 🡪 sk = 1.414x10-4 g
* Mass of Iron sampleerror sI2= (.0001)2 + (.0001)2 🡪 sI = 1.414x10-4 g
* Volume K2Cr2O7 used error sv2= ((.00002)2+.000022)1/2 🡪 sv =2.828x10-5 L
* Moles K2Cr2O7 error sm2= (sk2)1/2g -🡪 sm =4.808 x 10-7
* Molarity (moles/volume) K2Cr2O7 error (smo /molarity K2Cr2O7)2= (sm/m)2 + (.0002/.5)2 🡪smo = 8.07x10-6 mol/L
* Moles K2Cr2O7 used error (st /moles K2Cr2Oused)2= (smo /molarity K2Cr2O7)2 + (sv /.03660L)2 🡪 st = 1.118x10-5 mol
* Mass Fe titrated error sf = st =.003746 g
* % Fe used error (sp /%mass Fe)2= (sf /mass Fe)2 + (sI / .4500g)2=.1154 %

**Discussion:**

This graph of an acid-base titration of pH vs. Volume of solution added (4) shows a titration curve of an acid with a base (alkali). The equivalence point is at a certain volume of base, and, at that volume, movement on the x-axis in either direction causes a drastic change in pH (–log[H+]). The rate at which the redox reaction occurs begins slowly, but accelerates rapidly as the endpoint (or equivalence point) is approached, so the determination of the concentration of the solution requires great accuracy and precision.



The initial conversion of Fe3+ to Fe2+ relies on the reducing power of Sn2+, which, due to its level of selectivity for Fe3+, will reduce it. Under standard conditions, the formal potential (Eo) for the reduction of dichromate to chromic ions and oxidation of Fe2+ to Fe3+ are, respectively, +1.33 V and -.77 V (2). In the presence of 1 M HCl, they are, respectively, +1.00 V and -.70 V. Finally, in the presence of the phosphoric-sulfuric reagent, the Fe2+ half-reaction is -0.61 V to make the net +.39 V, which is closer to that of the equivalence point of the conversion of diphenylbenzidine to diphenylbenzidine-violet (+.87 V). The sum of these two potentials is positive, so it is energetically favorable.

Redox (“reduction-oxidation”) reactions involve the transfer of electrons to give new atomic charges to the species involved in the reaction. Iron commonly exists in two oxidized states (2+ of FeO and 3+ of Fe2O3). Reducing agents are oxidized to lose electrons, while oxidizing agents are reduced to gain electrons. In the titration reaction, Fe3+ is the oxidizing agent and Cr2O72- is the reducing agent. Transferring electrons also changes the properties of elements and compounds, such as the change from Fe3+ (yellow in the presence of chloride ions) to Fe2+(colorless). This change allows us to observe when the reaction has occurred and gone to completion. Titration, or, quantitatively determining the concentration of a given volume of a solution, of a redox reaction and calculations determine the percent iron in the sample. If the volume of a solution of known concentration necessary to drive a reaction to completion is determined, the number of moles of that molecule (dichromate) can be determined. From this number of moles, the number of moles of the molecule to be determined (iron) can be calculated, and the mass and percent mass can, therefore, be calculated. In order to determine when the reaction has reached completion, a few drops of an indicator are added to the solution prior to titration. This indicator, usually one that reacts reversibly with the ions that are produced form the titration reaction, changes color over the standard potential of the end of the reaction to show that the reaction has gone to completion. The reversibility of the behavior allows it to change colors slightly to the endpoint color (violet) but revert back to the original color as the endpoint is approached and, finally, change color permanently as the endpoint is reached. The endpoint is reached when enough reactant is added to reach completion of the reaction.

Our results indicate reasonably good accuracy. The results of our trials were close to each other and to the actual Fe%. Our percent error of 2.43% is relatively small, but not incredibly accurate. Our trials were consistently above the average, indicating that we may have added too much dichromate during titration. If we mistook the endpoint color for the wrong shade of violet, we may have titrated the dichromate with the iron past the endpoint color and caused a greater dichromate volume to be used. This hints that there may have been a systematic error. This would increase the iron mass and percentage. The initial volume of the burette may have been incorrectly read as zero instead when there was dichromate in the tip of the burette. The burette’s initial reading of zero may have been taken incorrectly, and the initial reading may have been greater than zero. The burette might not have been calibrated correctly, producing volumes results consistently too large.

The error propagation allowed us to measure the degree of random error that can be used to measure the uncertainties of our data due to the precision of the instruments in the lab. This gives us a context for to put our data in when comparing to the results from other similar experiments performed by others. Error propagation combines uncertainties from different measurements (e.g., multiplying a volume by molarity). Given that all of our variables were independent of one another, the calculations involving multiplication and division were in a similar form, and the ones involving addition and subtraction were in another similar form. This has applications in professions involving the analysis of the precision and accuracy of scientific instruments and the statistical analysis of scientific data to arrive at conclusions.

Titrations can be used to figure out the concentrations of unknown samples in fields of forensics, medicine, engineering, and winemaking. The concentrations of molecules give information of how the sample will react and what has occurred to the sample. For example, in the production of biodiesel fuels, the amount of base catalyst KOH needed to react with waste vegetable oil can be determined by calculating the acid concentration of the waste vegetable oil via titration (3). The lab could be improved with more time and materials to allow more trials to be carried out (especially since some materials were not as readily available due to stock-room mistakes). This would allow a more accurate average to be obtained.

**Conclusion:**

This experiment fruitfully determined the percent iron in the iron sample by titration. Despite the color change of the conversion of dichromate (orange) to chromic ions (green), the diphenylbenzidine is added to make the color change sharp and noticeable because the endpoint would be masked by the dichromate otherwise. Dichromate is a good oxidizing agent due to the electronegativity of the oxygen atoms and the capability of the chromium ions in it to be reduced. The chromium ions can be reduced since they exist in a +6 state in dichromate, but can favorably exist as 2+ or +3 (in Cr3+).

Though we did not investigate the pH of our solution, a graph of vs. Volume of solution added and a graph of –log[H+] vs. Volume of solution added would be similar. The is the standard potential of the reaction, which, in our case of a redox reaction, would be the movement of electrons from the reducing agent (Fe2+) to the oxidizing agent (dichromate). This movement of charge corresponds to a change in acid concentration, which corresponds to a change in H+ concentration. Hence, is directly proportional to pH.

Sources

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