# KANSAS GEOLOGICAL SURVEY ANALYTICAL SERVICES LABORATORY
## Water Analyses

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## General Considerations

Upon receipt, all samples are logged into the laboratory's master logbook. Pertinent information is then transferred to project data sheets (paper files) and to electronic project files. Surface-water samples and most ground-water samples not derived from irrigation or other high-capacity wells require filtration through a 0.45-micron filter membrane. This can take from about 3 minutes to well over an hour in order to obtain a sufficient amount of sample for the analytical work requested. If cations or nutrient species have been requested, a 100-ml aliquot of the sample is acidified with 1ml 6M HCl. All samples are then refrigerated until analytical work is begun.

Upon completion of the requested analytical work, electronic transfers of completed data sets are made to appropriate individuals. Relevant data are then added to a Chemical Quality file, which is used in the estimation of concentration levels for the preparation of dilutions for various analyses. Figure 1 provides a general overview of the sequence in which requested data are generated. It also reflects the application of various analytical results to subsequent determinations.

## Instrumentation

The following list gives the instrumentation employed by the Kansas Geological Survey (KGS) Analytical Services Laboratory in the analysis of surface- and ground-water samples.

1. Lab-Line Instruments Lectro Mho-Meter: Specific Conductance
2. Fisher Titration II System: pH, $CO_3^{-2}$, $HCO_3^-$
3. Hach One Laboratory pH/ISE Meter & Electrodes: $F^-$
4. Alpkem Flow Solution IV System: $Cl^-$, $SO_4^{-2}$
5. Technicon AutoAnalyzer II System: $NO_3^-$-UV, $Br^-$, $I_{Total}$, $IO_3^-$-I, $NH_4^+$, $PO_4^{-3}$
6. Jarrell-Ash Model 975 Plasma AtomComp with MARKII/MARKIII Update Kit: Ag, Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Na, Ni, Pb, Se, Si, Sr, Ti, V, Zn, K
7. Hach DR-700 Colorimeter: Turbidimetric $SO_4^{-2}$ (for oil brines)

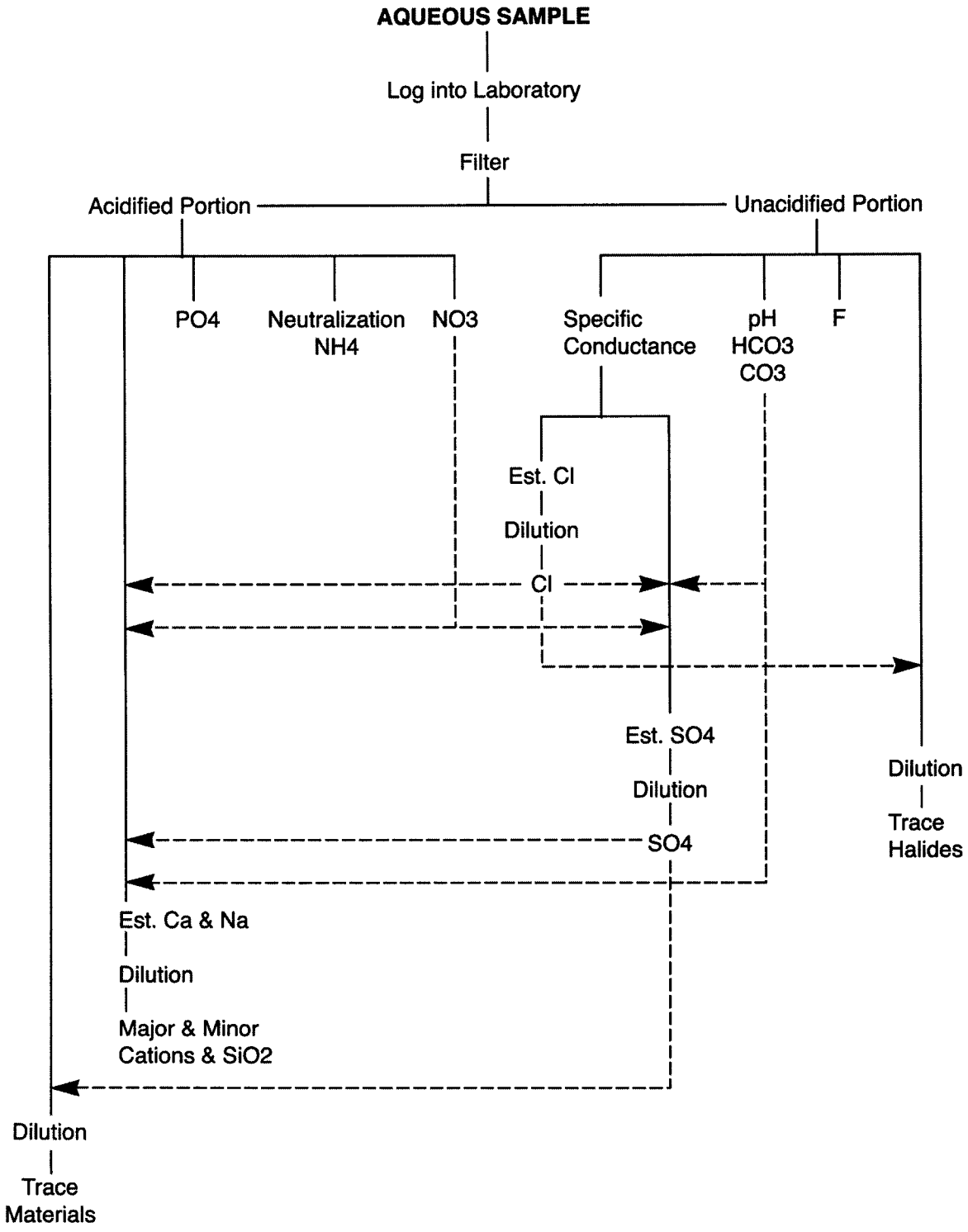


Figure 1. General Analytical Scheme for Water Samples

## Analytical Methodologies

1. Specific Conductance:
   The Lectro Mho-Meter spans three ranges: 1-100 $\mu$ mhos, 100-10,000 $\mu$ mhos, and 1,000-100,000 $\mu$ mhos. The middle range is automatically compensated for temperatures differing from 25°C, but the other two ranges require manual adjustment for temperature and/or cell response differences.

2. pH-Alkalinity ($CO_3^{-2}$, $HCO_3^-$):
   The Fisher Titration II System is a dual end-point titrimeter unit. The end-points set on the system are pH 8.3 ($CO_3^{-2}$) and pH 4.5 ($HCO_3^-$). Calibration of the system is achieved using buffer solutions of pH 4 and 7. A commercial 0.02 N $H_2SO_4$ solution is used as the titrant. The exact normality of the acid solution is determined by the titration of known amounts of $NaHCO_3$.

3. $F^-$:
   Fluoride determinations are made using the Hach One Laboratory pH/ISE Meter in conjunction with a fluoride ion-selective electrode and appropriate reference electrode. Samples and calibration standards are treated with an ionic strength buffer solution prior to analysis. A six-point calibration curve covering the range of 0.1-5.0 ppm $F^-$ is used in conjunction with the "built-in" 4$^{th}$-order curve-fitting program of the Hach unit to evaluate unknowns. A calibration standard is run at the beginning of a series of unknowns, after every 10 unknowns, and at the end of the series of unknowns.

3. $Cl^-$ and $SO_4^{-2}$:
   The Alpkem Flow Solution IV System is an automated unit which is fully under computer control for its operation and data reduction. It employs a UV-Vis spectrophotometer as the detector. Seven calibration standards are used to cover the concentration range of 0-200 ppm for both ionic species. Calibration standards are run in triplicate at the beginning of each run, and a calibration standard and two blanks are run after every 10 unknowns and/or at the end of the analytical run. A 3$^{rd}$-order fit of the calibration data is used to generate the calibration curve for the 0-200 ppm range. The calibration curve is broken down into 4-point segments for data reduction of unknown samples. The system's WinFLOW V3 Software corrects for baseline drift over the course of the analytical run.

4. $NO_3^-$-UV, $Br^-$, $I_{Total}$, $IO_3^-$-I, $NH_4^+$, $PO_4^{-3}$:
   The Technicon AutoAnalyzer II System also has a UV-Vis spectrophotometer as the detector unit, but employs a strip-chart recorder to record peak heights. These strip charts must be evaluated by hand. In doing so, corrections are made as needed for baseline drift and changes in analytical sensitivity over the course of a run.

Determinations made on the Technicon system employ 6-8 calibration points to generate the respective calibration curves. A set of calibration standards are run at the beginning and the end of each analytical run, and a calibration standard and two blanks are run after every 10 unknown samples. A 2nd-order fit of the calibration data is used to generate the calibration curve. The curve is broken down into 3-point segments for the evaluation of data from unknown samples.

5. Ag, Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Na, Ni, Pb, Se, Si, Sr, Ti, V, Zn, K:
   The Jarrell-Ash Model 975 Plasma AtomComp with MARKII/MARKIII Update Kit (hereafter referred to as ICP unit) was designed for the analysis of natural surface- and ground-water samples. In initial evaluation of the unit, it was noted that curvature was present in the 0-100 ppm range for Ca and Na and in the 0-20 ppm range for Mg and K. Other elements appeared to have relatively linear curves over the dynamic ranges of interest. A 9-point calibration curve was determined for the four elements above and was stored in the operating system of the ICP. The average of six consecutive burns is employed in data reduction for blanks, standards, and unknowns. A blank and the highest calibration standard are used to calibrate the unit before each set of unknowns. Unknowns are run in groups of three, followed by the high-calibration standard. The responses of the calibration standards are used to make any necessary adjustments to the data for the intervening unknowns due to sensitivity shifts. If the values derived for the high calibration standard vary by more than ±2%, then the system is recalibrated and the affected samples are rerun. If the statistical variation for the six sample burns exceeds 2%, the run is stopped and the torch and nebulizer unit are cleaned.

6. Turbidimetric $SO_4^{-2}$:
   A Hach DR-700 Colorimeter is used to measure $SO_4^{-2}$ in oil brines or oil-brine contaminated water samples. It has been noted that some of these brine-related sample types may contain components which produce interferences in the colorimetric method employed with the Alpkem system, and a 2nd-order curve fit is used to evaluate analytical data.

## Quality Aspects

1. Reference standard log files are maintained for ion-selective electrode and Technicon-based determinations. In each case the measured value of the standard is recorded for each analytical run. These responses are evaluated to detect potential problems with instrumentation, reagents, or calibration standards.

2. In all cases, over-range samples are diluted so that final determinations are made from measurements obtained within the limits of the respective calibration curves.

3. Determined values for calibration standards distributed throughout the Alpkem, Technicon, or ion-selective electrode analytical runs of unknowns serve as a quality-control measure.

4. For those samples where a complete set of major cation and anion determinations have been requested, it is possible to carry out a charge balance check for deviation from electroneutrality. It is assumed that quality control has been achieved if the sum total difference between positive and negative charged species is ±0.25 meq or ≤ 2% of the total meq level of the sample, whichever is the lesser value. If samples exceed these limits, they are re-examined.

5. Another form of quality evaluation is the participation in the USGS's Analytical Evaluation Program for Standard References Samples. Twice a year about 100 laboratories analyze sets of samples in this program and submit their results to the USGS for a statistical evaluation. Scores on individual determinations range from 0-4 (Unsatisfactory-Marginal-Satisfactory-Good-Excellent), and are based upon the number of standard deviations that the reported value differs from the most probable value (MPV) for that component. KGS average scores on the Major Component Samples for the period 2000-2003 (M-154, M-156, M-158, M-160, M-162, M-164, M-166 and M-168) are given below.[1-8] KGS is Laboratory 24 in the USGS reports. Beginning with the Fall 2003 set of samples, paper reports will be replaced by electronic reports. The specific conductance of this sample group varied from 182-1124 $\mu$ mhos.

| | |
|---|---|
| Alkalinity | 4.0 |
| B | 3.9 |
| $Ca^{+2}$ | 3.8 |
| $Cl^{-}$ | 3.8 |
| $F^{-}$ | 4.0 |
| $K^{+}$ | 3.6 |
| $Mg^{+2}$ | 3.4 |
| $Na^{+}$ | 3.8 |
| pH | 3.5 |
| $SiO_2$ | 2.8 |
| $SO_4^{-2}$ | 3.1 |
| Specific Conductance | 3.6 |
| $Sr^{+2}$ | 3.5 |

Three of the Major Component Samples (M-162, M-164 and M-168) had specific conductance values which were below 400 $\mu$ mhos, and were generally considered to be non-representive for the sake of comparison to the analysis of Kansas ground-water

samples. The data from these samples were eliminated, and those of the remaining five samples, with a specific conductance range of 432-1124 $\mu$ mhos, were used to evaluate standard deviations and percent deviation for the constituents determined. Standard Deviations were determined from the KGS-MPV ranges for the five standard samples under consideration. The Percent Deviation was calculated by averaging the comparisons of absolute KGS-MPV ranges to the respective MPV values. These quantities are summarized below.

| Determination | Standard Deviation | Percent Deviation |
|---|---|---|
| Alkalinity | ±0.6 ppm | 1.0 % |
| B | ±2.0 ppb | 4.0 % |
| $Ca^{+2}$ | ±0.3 ppm | 0.9 % |
| $Cl^{-}$ | ±0.9 ppm | 1.3 % |
| $F^{-}$ | ±0.011 ppm | 3.5 % |
| $K^{+}$ | ±0.05 ppm | 2.7 % |
| $Mg^{+2}$ | ±0.2 ppm | 1.7 % |
| $Na^{+}$ | ±1.5 ppm | 2.0 % |
| pH | ±0.07 units | 0.9 % |
| $SiO_2$ | ±0.4 ppm | 5.4 % |
| $SO_4^{-2}$ | ±1.6 ppm | 2.5 % |
| Specific Conductance | ±8 $\mu$ mhos | 1.3 % |
| $Sr^{+2}$ | ±0.012 ppm | 3.1 % |

These approaches provide a general appreciation for the uncertainty associated with the respective analyses of water samples in the KGS laboratory. It should be kept in mind that these results have been obtained by vigorous attempts to operate in the middle regions of the appropriate calibration ranges whenever possible. Operation at the extremes of the calibration ranges may lead to significant deterioration in quality of data produced.

## References


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