

BOARD OF WATER ENGINEERS

Austin, Texas

INTEROFFICE MEMORANDUM

To: L. G. McMillion

Date: April 4, 1960

From: F. A. Rayner

Subject: Mathematical method of comparing chemical analyses.

The following dissertation concerning a mathematical method of comparing chemical analyses was first compiled January 9, 1960, submitted to your office February 13, 1960, for typing (refer to my memorandum of February 13, and your memorandum of February 19), and is herewith resubmitted.

Pursuant to our conversation of March 4, I will, at a later date, condense this paper, removing "personalities" and reference to specific contamination cases, for submission to the consulting field for review and use.

A MATHEMATICAL METHOD OF COMPARING CHEMICAL ANALYSES

After making the Odessa Auto Auction Company contamination investigation, my second such case, I have given considerable additional thought to chemical changes in contaminated ground water.

The dissimilarity in the quality of the contaminated water encountered in the Leland Davison contamination case, North Welch Oil Field, Dawson County, and the Odessa Auto Auction Company contamination case, Midland County, has prompted me to revive and revise a mathematical method of chemical analyses comparison, which I developed while working on the L. Davison case. This suggested method for comparing chemical analyses was not included in my report of the L. Davison case, as submitted to your office, because of the voluminous dissertation connected therewith.

METHOD OF COMPARISON

The element chlorine (chloride) was used as a control element, because of the relative stability of this element in solution, and the ease and accuracy with which it can be separated and/or measured within a wide range of solution concentrations.

CONTAMINATED WATER, ODESSA AUTO AUCTION COMPANY

The contaminated water, encountered in the Odessa Auto Auction contamination investigation, contained considerable sodium (value of sodium + potassium was assumed to have been determined by analysis, and is not a calculated value; potassium was considered negligible, or less than 230 ppm) as exemplified in Table 1 below.

Table 1:

Chemical analysis of water from Odessa Auto Auction Company well No. 14, Midland County, in ppm. Sample collected November 21, 1959, by the Western Company, Midland, Texas.

Sodium+Potassium	Calcium	Magnesium	Chloride	Bicarbonate	Sulfate
2,185	416	76	3,020	305	700

If the sodium (+ potassium), listed in Table 1, is a measured value, it is obvious that there is enough sodium in this sample to combine with all the chloride present.

An analysis of the fluids produced and disposed into a nearby salt-water and B. S. disposal pit, by Plymouth Oil Company's Fourdree "G" No. 1 oil well, is not available (readily), however, it is logical to assume that fluids produced by this well were high in sodium and chlorine. (see my report on the Odessa Auto Auction Company contamination investigation, December 14, 1959).

CONTAMINATED WATER, TED TURNER'S HOUSE WELL

A sample of water collected from Ted Turner's house well, No. 14-6, (see maps in my report on the Ieland Davison contamination investigation), on June 22, 1957, was analyzed by Goodpasture Laboratories, Brownfield, Texas; the results of this analysis are listed in Table 2 below.

Table 2:

Chemical analysis of water from Ted Turner's house well, No. 14-6. Sample collected June 22, 1957. Analysis by Goodpasture Laboratories, Brownfield, Texas.

Bicarbonate	Sulfate	Chloride	Calcium	Magnesium	Sodium	Potassium
110	472	550	20	224	160	30

For the purposes of this comparison the quality of the water from this well (Ted Turner's house well), at the time the sample was collected, will be considered as the quality of the uncontaminated water in the vicinity of the subject well, however, it is obvious that some degree of contamination had already taken place before this sample was collected.

Table 3 depicts the quality of a sample of water taken from this same well (No. 14-6) exactly 25 months later.

Table 3:

Chemical analysis of water produced from Ted Turner's house well, No. 14-6, in ppm. Sample collected July 22, 1959. Analysis by the U. S. Geological Survey.

Anion		Cation	
Calcium -	345	Bicarbonate -	246
Magnesium -	425	Sulfate -	662
Sodium -	369	Chloride -	1,850
Potassium -	40		

The quality of the water produced by the eight oil wells on the W. J. Burkett lease, which was disposed in the W. J. Burkett salt-water, B. S. disposal pit located near Ted Turner's wells (Nos. 14-5 and 14-6, see maps in the before mentioned report), is very similar in quality, therefore, an analysis of the fluids produced by the W. J. Burkett No. 6 oil well will be considered as typical of the fluids that were disposed into the subject salt-water, B. S. disposal pit.

Table 4:

Chemical analysis of fluid produced from the W. J. Burkett No. 6 oil well, in ppm. Analysis made February 12, 1958, by the Tretolite Company.

Chloride	Sulfate	Calcium	Magnesium	Sodium
41,900	4,400	3,600	170	23,764 <sup>1/</sup>

As NaCl = 63,800 ppm.

<sup>1/</sup> - Calculated as follows:

Atomic weight of Cl = 35.457, of Na = 22.997.

$22.997/35.457 = .648$  parts Na to Cl.

$(.648) (41,900) = 27,200$  ppm Na, which combined would equal 69,100 ppm NaCl, however, the probable value of NaCl = 63,800 ppm, or a difference of 5,300 ppm.

Applying the same ratio,  $(.648) (5,300) = 3,436$  Na not available, therefore,  $27,200 - 3,436 = 23,764$  ppm Na available.

Comparing the chloride concentration in a sample of water taken from the Ted Turner house well, 14-6, on June 22, 1957 (see Table 1), to the chloride concentration in a sample of water taken from this same well, on July 22, 1959, disclosed a chloride increase of 1,300 ppm (see Table 3).



Assuming that this increase in chlorides was wholly derived from the fluids disposed in the nearby salt-water, B. S. disposal pit (see Table 4), there has been, as of July 22, 1959, a dilution of 3.1% of the contaminating fluids, in the vicinity of well 14-6.

$$1,300/41,900 = .031 \text{ or } 3.1\%$$

A 3.1% dilution of the other elements (in actuality dilution of the solution in which the elements are present) in the contaminating water, would make available for contamination the amounts of the respective elements as listed in Table 5.

Table 5:

Elements available for contamination from Table 4.

Element (1)	Original Concentration ppm. (2)	Dilution (3)	Available for Contamination, ppm (2x3)
Chloride	41,900	.031	1,300
Sulfate	4,400	.031	136
Calcium	3,600	.031	111
Magnesium	170	.031	5
Sodium	23,764	.031	736

The change in concentration of the respective elements, in the contaminated water, is algebraically compared with the available concentrations of the same elements from the assumed contaminating source in Table 6.

Table 6:

Comparison of concentration of elements, in ppm, in contaminated and contaminating fluids. Developed from Tables 2, 3 and 5.

1	2	3	4	5	6
Element	Original Concentration ppm	Present Concentration ppm	Change in Concentration ppm (3 - 2)	Available for Contamination ppm	Difference ppm (5 - 4)
Bicarbonate	110	246	136		
Sulfate	472	662	190	136	-54
Chloride	550	1,850	1,300	1,300	Control element
Calcium	20	345	325	111	-214
Magnesium	224	425	201	5	-196
Sodium	160	369	209	736	527
Potassium	30	40	10		

Disregarding other factors, to be discussed later, Table 6 indicates that if the oil well fluid, disposed in the nearby salt-water disposal pit, is the source of the contaminant, this same fluid possesses a deficiency in three elements, sulfate, calcium and magnesium, while being able to supply 527 ppm more sodium than is actually in the contaminated ground water.

Table 6 also indicates that chlorides in water produced from well 14-6 increased by 1,300 ppm, while the sodium content therein only increased by 209 ppm.

Santa Rosa Fluids

Using the same method of analytical comparison heretofore discussed, the possible contaminating Santa Rosa fluids are compared below:

Table 7:

Chemical analysis of water produced from the Santa Rosa Sand, by a well located about 13 miles southwest of well No. 14-6, in ppm. Sample collected December 19, 1958, by the Pan American Petroleum Corporation.

Anion		Cation	
Chloride -	4,964	Sodium -	4,261
Sulfate -	3,347	Calcium -	381
Bicarbonate -	598	Magnesium -	186
Carbonate -	0		

If Santa Rosa water, containing dissolved solids in quantities as listed in Table 7, is the contaminant (see L. Davison report for method), the effective dilution, using chloride as a base element, is 26.2%.

$$1,300/4,964 = .262 \text{ or } 26.2\%$$

Table 8:

Elements available for contamination, in ppm. From Table 7.

Element (1)	Original Concentration ppm (2)	Dilution (3)	Available Concentration ppm (2x3)
Chloride	4,964	.262	1,300
Sulfate	3,347	.262	877
Bicarbonate	598	.262	156
Carbonate	0	.262	0
Sodium	4,261	.262	1,115
Calcium	381	.262	100
Magnesium	186	.262	49

Table 9:

Comparison of concentration of elements, in ppm, in contaminated and contaminating fluids. Developed from Tables 2, 3 and 8.

1 Element	2 Original Concentration ppm	3 Present Concentration ppm	4 Change in Concentration ppm (3-2)	5 Available for Contamination ppm	6 Difference ppm (5-4)
Bicarbonate	110	246	136	156	20
Sulfate	472	662	190	877	687
Chloride	550	1,850	1,300	1,300	Control Element
Carbonate		0	0	0	
Magnesium	224	425	201	49	-152
Calcium	20	345	325	100	-225
Sodium	160	369	209	1,115	906

A preliminary analysis of the data in Table 9 indicates a wider discrepancy in comparing the Santa Rosa water to the contaminated water, in as much, as there is no pattern in the surpluses or deficiencies of elements in this assumed contaminating source. There is a notable surplus of sodium and sulfate in the Santa Rosa water that did not appear in the contaminated water.

#### Cretaceous Fluids

The only remaining suggested source for the contaminating fluids, in the L. Davison case, is the Cretaceous sands, penetrated by Ted Turner's abandoned irrigation well, No. 14-5, located about 600 feet to the northeast of well No. 14-6 (see maps in the Leland Davison report).

Since water produced from the abandoned irrigation well, No. 14-5, reached a chloride concentration up to 4,000 ppm, it would be necessary for the contaminating source to supply fluids containing approximately 3,450 ppm chlorides, neglecting dilution and assuming an original concentration of 550 ppm chlorides in the ground water in this area (estimate of 550 ppm chloride is known to be excessive, but is used here for comparison purposes, see Table 2).

The wells used for this comparison are the nearest Cretaceous penetrating wells, except well 14-5, to well 14-6. Both of these wells are located near large alkaline lakes, which contained highly mineralized water.



Table 10:

Chemical analysis of water produced from a well penetrating Cretaceous deposits, located about 11 miles east northeast of well No. 14-6, in ppm. Well No. 33, from Dawson County Report, 1938.

Anion		Cation	
Chloride	- 3,325	Sodium + Pot.	- 589 <u>1/</u>
Sulfate	- 923	Calcium	- 318
Bicarbonate	- 226	Magnesium	- 179

1/ Considered as all sodium.

Table 11:

Chemical analysis, in ppm, of water produced from a well penetrating Cretaceous deposits, located about 23 miles north northwest of well No. 14-6. Well No. 70, from Terry County Report, 1944.

Anion		Cation	
Chloride	- 7,570	Sodium + Pot.	- 3,941 <u>1/</u>
Sulfate	- 365	Calcium	- 598
Bicarbonate	- 85	Magnesium	- 259

1/ Considered as all sodium.

If water of the quality as listed in Table 10 in the contaminating fluid, there has been a 39.1% dilution of this contaminant.

$$1,300/3,325 - .391 \text{ or } 39.1\%$$

Contaminating fluids of the quality listed in Table 11, would represent a dilution of 17.2%.

$$1,300/7,570 - .172 \text{ or } 17.2\%$$

The concentrations of available contaminants, as related to the two subject sources (water qualities), compared with the change in element concentrations in the contaminated water, are listed in Table 12.

Table 12:

Concentration of elements available for contamination, compared with the change in element concentrations in the contaminated water.

Element, in ppm

	From Table	Chloride	Sulfate	Bicarb.	Sodium	Calcium	Magnesium
Original Concentration (1)	10	3,325	923	226	589	318	179
	11	7,570	365	85	3,941	598	259
Dilution (2)	10	.391	.391	.391	.391	.391	.391
	11	.172	.172	.172	.172	.172	.172
Available Concentration (3)	10	1,300	360	88	230	123	70
	11	1,300	63	15	670	103	44
Change in Concentration (4)	6						
	or 9	1,300	190	136	209	325	201
Difference (3-4)	10	Control	170	-48	21	-202	-131
	11	Element	-127	-121	461	-222	-157

Table 12 indicates that the contaminating source could have been similar in quality to the water whose analysis appears in Table 10, if the criteria for recognizing such similarity is the element sodium. It is necessary to recognize that this source contained only 3,325 ppm chlorides (undiluted) and, therefore, can not be recognized as the contaminating source (see page 8).

The comparison, Table 12, of both of the Cretaceous fluids considered revealed anomalies, to be discussed later, that eliminates the recognition of these fluids as the contaminating source.

EFFECT OF CONDUCTING MATERIAL

Sand sections, particularly uncemented, relatively silt free Ogallala sands, should not produce any notable chemical changes in a fluid passing through such a conduit, because of the relatively inert quality of the quartzitic sands (SiO<sub>2</sub>) in the subject areas.

It is reasonable to assume that any contaminant directly entering these sands (through a well bore) should not experience any notable ionic exchange with the sand media, and would, therefore, appear in a contaminated well relatively unchanged except for dilution.

The Cretaceous sands, in the subject areas, are probably calcareously cemented, and would, therefore, be expected to cause a change in the chemical quality of any foreign fluid entering these sands.



Oil well fluids disposed in the W. J. Burkett salt-water, B. S. disposal pit, (see the L. Davison report) would necessarily have to filter downward through an extensive, (40 feet or more) permeable caliche deposit, before reaching the water saturated sands in the vicinity of wells 14-5 and 14-6.

A similar situation probably exists beneath the salt-water, B. S. disposal pit in the area of Plymouth Oil Company's Foudree "G" No. 1 oil well. It is quite possible that fluids disposed in this pit would have to filter downward through a Cretaceous limestone section, before entering the water bearing sands in this portion of Midland County.

Oil field brines moving through caliche and/or limestone sections, like those below the above mentioned salt-water disposal pits, would undergo chemical changes resulting in the loss and/or gain of certain elements. (see later text)

#### PROBABLE CHEMICAL CHANGES

If the contaminating source, in the L. Davison case, are fluids from the Santa Rosa sands, it would be necessary for these fluids to move upward in an oil well bore and enter the Ogallala sands directly, or the Cretaceous sands to ultimately enter the Ogallala sands through well 14-5. The probability of the contaminants entering the fresh water aquifer (Ogallala) via well 14-5 can be disregarded by referring to data presented in the L. Davison report.

Therefore, if Santa Rosa water is entering the Ogallala sands, this contaminant should appear in the contaminated water wells unchanged except for dilution.

Referring to Table 9, a comparison of the contaminated water and the Santa Rosa fluids, reveals a notable difference in the concentration of elements in the contaminated water, and the concentration of elements available for contamination from the Santa Rosa water. There is a large excess of sodium and sulfate available in the contaminant, which does not appear, in a similar magnitude, in the contaminated water.

Adding, algebraically, the difference (column 6, Table 9) in the concentration of elements of the contaminant and contaminated water, revealed an excess of 1,230 ppm dissolved solids in the contaminant, which did not appear in the contaminated water.

$$\begin{array}{r} 20 \\ 687 \\ -152 \\ -225 \\ \hline 906 \\ \hline 1,230 \end{array}$$

Cretaceous fluids, native to these sands, should also enter the contaminated wells unchanged chemically.

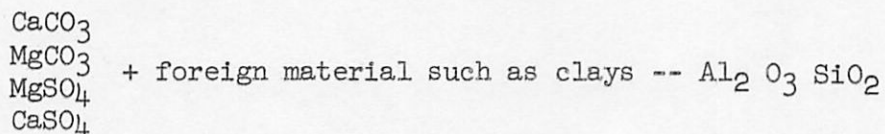
Algebraically comparing the difference in the available element concentrations in the contaminated water with similar element concentrations in the considered water qualities, depicted by Table 10 and 11, indicated a deficiency of 190 and 166 ppm (dissolved solids), respectively, in the two considered contaminating sources (water qualities).

170	-127
-48	-121
21	461
-202	-222
<u>-131</u>	<u>-157</u>
-190	-166

Water of the quality depicted by Table 11 was deficient, as a contaminant, in all elements except sodium, of which it contained an abundance, a relationship that would require further study if this water was entering the fresh water aquifer from the surface. (see later text)

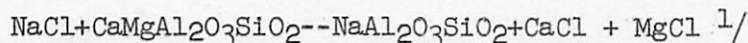
Brine disposed in surface pits would be expected to experience a change in chemical composition while filtering downward through caliche and/or limestone deposits, until a quantity of such a solution had passed through these calcareous deposits that equilibrium (chemical) would be established between the fluid, and the conducting material.

Considering the basic or general composition of caliche, the following compounds could be expected to be present in varying amounts.



It is readily evident that these deposits can be selectively recognized as "dead" zeolites, in as much as the compounds present are similar to a zeolite that has functioned to "soften" water (remove calcium and magnesium).

Zeolites are "charged", returned to their near normal or working state, by passing a brine (NaCl) solution through the grains of zeolite, which in solution proceeds basically as:



It is reasonable to expect a similar exchange of elements when a concentrated salt-water solution is allowed to filter through a deposit (caliche) rich in calcium and magnesium. This would reduce the amount of sodium, while increasing the amount of the elements calcium and magnesium, in a contaminant.

Adding, algebraically, the difference in concentration of the respective elements in the contaminated water and the contaminating source (fluids disposed in the W. J. Burkett salt-water disposal pit), revealed a surplus of 63 ppm dissolved solids in the contaminant, which did not appear in the contaminated water (see Table 6).

1/ Valence was not considered, and no attempt was made to balance the general example equations.

$$\begin{array}{r} -54 \\ -214 \\ -196 \\ \hline 527 \\ \hline 63 \end{array}$$

The necessary sulfate could have been made available to the contaminant, by the exchange of one or more of the cations in the brine, for sulfate in the subject caliche deposit.

It is interesting to note that the algebraic comparison of the difference in the amounts of the respective elements in the contaminant, with the amounts of the respective elements in the contaminated water, produced (L. Davison case) the least sum (264% less than that of the next nearest comparison) of all the considered sources.

This chemical exchange between the contaminating fluids, and the material (caliche) through which they pass, would be expected to continue at a diminishing rate, until enough fluid has passed through such a conduit to establish chemical equilibrium between the brine and the caliche. The time necessary to establish this equilibrium would depend on many factors, temperatures, quantities, chemical compositions etc., of the contaminant and the conducting material, however, for all practical purposes, equilibrium will be established only through time.

In the Leland Davison case, which was investigated soon after Mr. Turner's wells first became contaminated, the water sampled was water that had been contaminated, by a contaminant which was not in chemical equilibrium with the caliche deposit through which it had filtered.

Salt water disposed in the Plymouth Oil Company's salt-water disposal pit, on the Foudree "G" lease, would necessarily have to filter downward through a caliche deposit (of unknown extent), however, the contaminated water produced by the Odessa Auto Auction Company's water well, No. 14, (see the Odessa Auto Auction contamination report) was similar in quality (contained abundant sodium) to the expected quality of water contaminated by chemically unaltered oil field brines.

The contaminant entering well No. 14 must have been in equilibrium with its conducting material in order to enter the subject well unaltered (containing enough combining sodium), except for dilution.

The time elapse between the disposal of brines in a surface pit and the eventual analysis of water (contaminated) produced by a nearby water well was four months, in the L. Davison case, and a reported seven years in the Odessa Auto Auction Company case.

#### LIMITATIONS

There are many factors that could severely restrict or render totally invalid, this type of chemical analyses comparison:

(1) Nonapplicability of the basic premise of this type of comparison. It is quite possible that there are factors limiting this method of analysis that are not included in, or known to the author at this writing. The use of



"reaction" values would possibly afford a better basis for comparison. This method of chemical analyses comparison could be improved by adjusting the base element, chlorine, before the percent dilution is calculated.

(2) Accuracy of the chemical analyses - any errors in the chemical analyses used would be magnified, since this is primarily a geometric comparison. Errors are inherent when analyses are made of very "weak" or very "strong" solutions. Calculated values, in the original chemical analyses, could not be used.

(3) Ionic attraction - if possible or applicable, adjustments would have to be made for ionic attraction between the contaminant and contaminated fluids, and the medium through which they move. This method of comparing chemical analyses could possibly be used to determine the amount of ionic attraction.

#### COMMENTS

(1) This method of chemical analyses comparison could be used to locate sources of contamination.

(2) With enough knowledge (chemical and physical) of the media through which the contaminating and/or contaminated water has passed, it is conceivable that time in or length of travel, of the contaminating or contaminated water, could be determined.

(3) The volume of contaminated water could be calculated, which in turn combined with geometric methods could be used to determine the boundaries of the contaminated area, as to specific water qualities.

(4) Predictions of the degree of deterioration in water quality could be made considering any given contaminant.

(5) The converse of the suggested uses, 2 through 4 above, could also be applied.

(6) The type and magnitude of remedial action (chemical, water flooding etc.) necessary to eliminate or restrict the effect of the contaminated or contaminating source could be determined.

(7) Areas of artificial or natural recharge could be located, particularly subsurface sources. A knowledge of the magnitude of such recharge could also be determined.

(8) The contaminating source, in the L. Davison case, is further affirmed as being the oil well fluids disposed in the W. J. Burkett lease, salt-water disposal pit.

(9) Any and all comments or suggestions regarding this method of chemical analyses comparison would be appreciated.

Note: Chlorine, chloride and chlorides were used interchangeably to denote chloride.