

DETERMINATION OF SOURCES  
OF SALINE WATER IN KANSAS BY  
BROMIDE AND IODIDE GEOCHEMISTRY

by

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## INTRODUCTION

### Purpose of Study

The problem of differentiating various types of natural waters has frequently been approached by interpretations of geochemical data (Carpenter, 1978; Collins, 1980). Examination of certain constituents and their ratios have produced correlations applicable in identifying the origin of other waters of similar nature, since like factors may govern their chemistry. Distinguishing water origin may be of interest in numerous situations, e.g. where more than one source of water is suspected.

The ability to distinguish saline waters by source is essential in the identification of saltwater contamination sources in groundwater or surface-water supplies. Numerous incidents of saltwater intrusion have occurred in both surface and subsurface waters in the State of Kansas.

Several sources exist for saline waters in the state. Three types of prevalent sources examined in this study are:

1. Oil-field brines;
2. Saline waters resulting from dissolution of Permian evaporite deposits;
3. Formation waters not associated with oil and gas, such as in shallow subsurface strata of the Cretaceous System.

The aims of this investigation were to:

1. Characterize, chemically, high-chloride waters from the three types of prevalent sources by determination of bromide and iodide and the ratios of these minor elements to chloride and sodium.
2. Ascertain whether this chemical characterization can be related to the salt-water source type.
3. Determine if the characterization of the saline source by these halogens can serve to differentiate origins of salinity for other natural waters.

In addition, sulphate and the major-cation constituents calcium, magnesium, sodium and potassium, together with lithium and strontium that occur as minor elements, were determined in order to characterize and compare the chemical nature of these waters, and in order to aid in the understanding of any processes possibly affecting chemical composition.

## Location of Study Areas

Oil-field Brines.--Selection of study areas was based on the availability of water samples representative of several petroleum-producing horizons. Sites chosen were not appreciably affected by secondary recovery and represented important producing zones in the state. Russell and Butler counties, two significant petroleum-producing areas, were selected for sampling. In addition, eight Ness County well waters, collected in September, 1977 for a strontium-isotope study at Kansas State University were analyzed for bromide, iodide, and chloride. Table 1 lists designation, legal description, and producing zones for oil-field brines sampled.

Russell County samples were collected from John O. Farmer leases near the city of Russell. In Butler County, secondary recovery of petroleum in strata of the Lansing-Kansas City Group is prevalent, and the brine sample was obtained from such an operation. All Butler County samples were taken from sites on Cities Service leases near Oil Hill, northwest of the city of El Dorado. All samples were collected from brine tanks. Ness County samples were collected at the wellhead from wells in the north-central region of the county.

Brines Associated with Permian Salt.--Salt has been commercially mined in the Hutchinson, Kansas area since the early 1900's. Regionally, documentation exists that groundwaters are also actively dissolving the formation, whose eastern margin underlies the Hutchinson area. Dissolution is causing deformation and collapse of overlying rock and damage to man made

Table 1. Sample information for oil-field waters

Identification	Location	Producing Zone and Description
	Russell County	
Erlich B(4)	Sec.30, T.14S., R.14W.	Arbuckle Group (Upper Cambrian-Lower Ordovician), "Gorham Sand" (Basal Pennsylvanian)
Erlich B(2)	Sec.30, T.14S., R.14W.	Arbuckle Group (Upper Cambrian-Lower Ordovician)
Sellens (F)	Sec.29, T.15S., R.13W.	Primarily Tarkio Limestone Member (Upper Pennsylvanian), some Lansing Group (Upper Pennsylvanian)
Rein	Sec.27, T.14S., R.13W.	Lansing Group (Upper Pennsylvanian). Primarily Lansing Group, some Tarkio Limestone Member and Arbuckle Group
Kuhnle Smoky Waterflood Unit	Sec. 4, T.15S., R.12W.	Primarily Lansing Group, a small amount of waterflood from Cedar Hills Sandstone (Lower Permian)
	Butler County	
-	Sec.25, T.25S., R. 5W.	Kansas City Group (Upper Pennsylvanian)
-	Sec.30, T.25S., R. 5W.	Viola Limestone (Middle Ordovician)
-	Sec.21, T.25S., R. 5W.	Arbuckle Group (Upper Cambrian-Lower Ordovician)
	Ness County	
Horchem DB-3	Sec.24, T. 5S., R.17W.	Cherokee Group (Middle Pennsylvanian)
Tilley 2	Sec.24, T. 8S., R.17W.	Fort Scott Limestone (Middle Pennsylvanian) and Mississippian System

Table 1. Sample information for oil-field waters (Continued)

Identification	Location	Producing Zone and Description
	Ness County	
Meyer DB-3	Sec. 15, T. 24S., R. 17W.	Cherokee Group (Middle Pennsylvanian)
Dickman 1	Sec. 17, T. 24S., R. 17W.	Mississippian System
Horchem AB-1	Sec. 34, T. 24S., R. 16W.	Cherokee Group (Middle Pennsylvanian)
Dickman 6	Sec. 17, T. 24S., R. 17W.	Mississippian System
Albers AB-4	Sec. 3, T. 24S., R. 17W.	Cherokee Group (Middle Pennsylvanian)
Horchem DB-1	Sec. 2, T. 24S., R. 17W.	Cherokee Group (Middle Pennsylvanian)

structures (Walters, 1976). Brines produced by solution mining were obtained through courtesy of Carey Salt, a Division of Interpace Corporation. Two brine wells, Numbers 82 and 98, were sampled at the mining and operations site in Hutchinson, Kansas. The wells produced from separate cavities and are approximately 600 ft apart. Carey operations force recirculated groundwater to the salt-bed base, and pressure of incoming water forces produced brine upward to settling tanks. The groundwater is obtained from five fresh-water wells located near the mining site. The wells draw water at a depth of 60 ft from the Arkansas River underflow.

A portion of a core from the Hutchinson Salt Member was dissolved in the laboratory and analyzed as a brine sample. The core was drilled from an abandoned Carey Salt Company mine near the town of Lyons in Rice County, during the Project Salt Vault Program conducted during 1965-1967. The sample was taken from the 1007 ft depth of a core stored at the Kansas Geological Survey.

The water from three wells producing from alluvium along the Smoky Hill River in Saline County was sampled (Fig. 1). These wells are part of a network of sites monitored in a continuing salinity study of the Solomon and Smoky Hill rivers, conducted by the Kansas Water Resources Board, the U.S. Geological Survey, and the Army Corps of Engineers. Although the region is hydrogeologically complex, the upwelling of saline groundwater from sites of Permian salt dissolution is known to contribute greatly to the salinity of the two rivers (Hargadine et al., 1979).

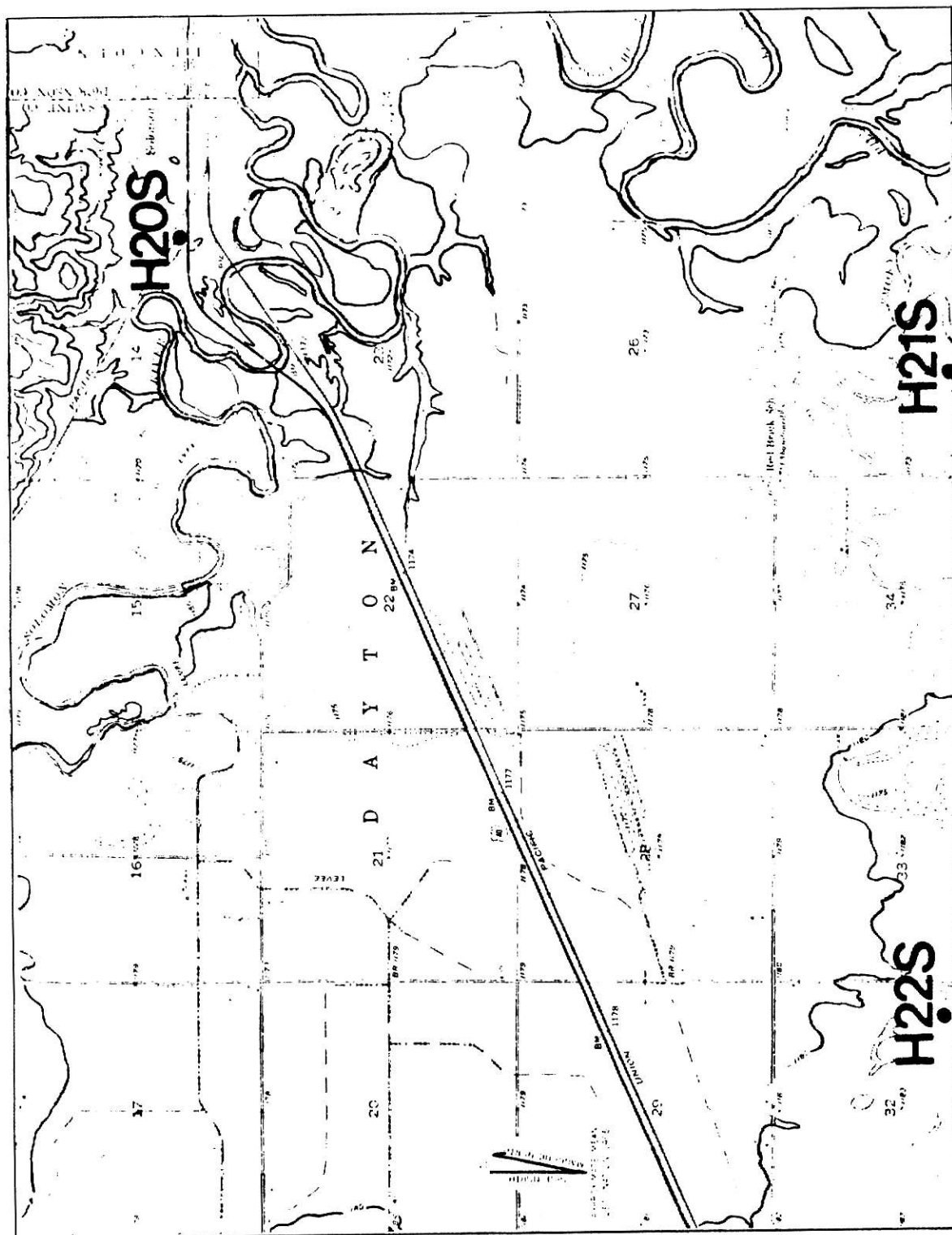


Figure 1. Sampling site of observation wells in Saline County, T.13S., R.1W. After U.S. Geological Survey 7.5 minute Series (Topographic), Niles Quadrangle, Kansas, 1955. Scale 1:38835.

Table 2. Sample information for observation wells,  
Saline County.

Identification	Location	Sampled Depth, ft below surface
"Railroad Triangle Well"	SW.1/4 NE.1/4 SW.1/4, Sec. 14, T.13S., R.1W.	50.0
"Dike Well"	SE.1/4 SW.1/4 SE.1/4, Sec. 35, T.13S., R.1W.	24.5
"Dead End Sign Well"	NW.1/4 SW.1/4 SW.1/4, Sec. 32, T.13S., R.1W.	29.3



Table 2 lists designation, location, and depth from which water samples were obtained.

Mineralized Waters Associated with the Dakota Formation.--

Because of difficulty of access to highly mineralized waters of the Dakota Formation, salt seepage contributed by this formation to surface water was sampled. Salt Creek flows for approximately three miles in Russell County northwest of the city of Russell (Fig. 2) where it joins the Saline River. Several salt seeps occur along the creek's course where Dakota rocks are exposed. Four stream-water samples were collected, representing a range of salinities.

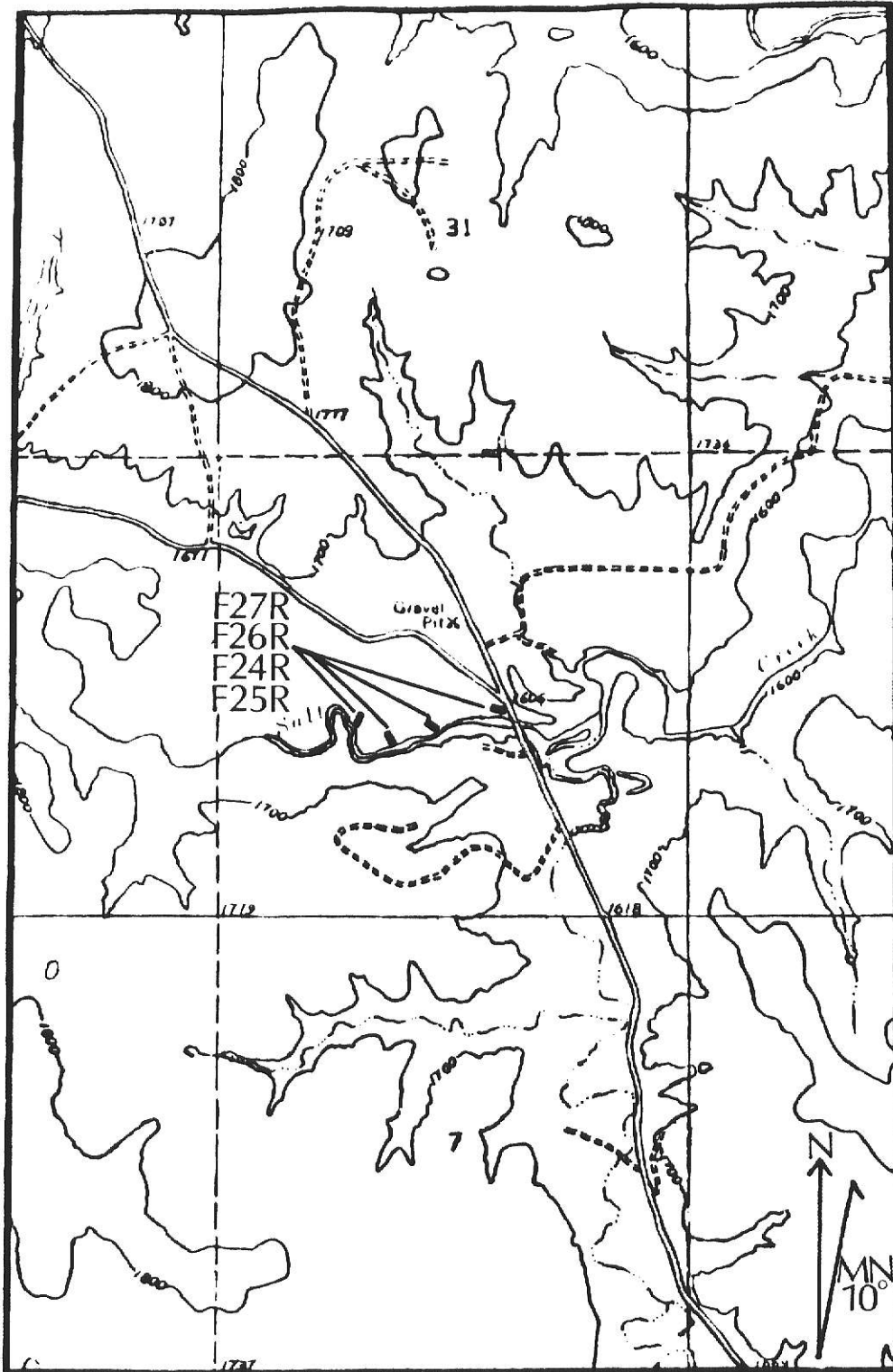


Figure 2. Sampling site of Salt Creek waters in Russell County, T.13S., R.14W. After U.S. Geological Survey 7.5 minute Series (Topographic), Russell NW Kansas Quadrangle, 1967. Scale 1:24000.

### Previous Investigations

Many investigators have studied the geochemistry of bromine, iodine, and chlorine in rocks, sediments, soil, and water. Correns (1956) presented available data on halogen distributions, citing volcanism as a major contributor of these halogens to the Earth's crust. No certain correlations were found to exist between halogen content and rock chemical composition or crystallization mode. Because of enrichment of these elements in seawater, the geochemical behavior in marine environments has been of considerable interest. Authors such as Tsunogai (1971) and Sugawara and Terada (1958) examined equilibrium reactions of iodine species in oxygenated seawater and the deep ocean. Numerous marine life forms are known to concentrate bromine and iodine (Low, 1949, and Baily and Kelly, 1955). The biogenic role of concentrating and recycling bromine and iodine in seawater and sediment profiles has been examined by Price and Calvert (1973, 1977), Gulyayeva and Itkina (1962), Price, et al. (1970), Tsunogai and Sase (1969), and others.

During the process of seawater evaporation, bromine and iodine do not form bromine or iodine minerals but are incorporated into salt-crystal structures by isomorphous substitution. Among studies of evaporite salt deposits are those of Kostenko (1974), Zak (1974), Krasintseva (1965), and Mun and Bazilevich (1963). Holser (1966) investigated these halogens in Permian salt near Hutchinson, Kansas.

Bromine and iodine distribution in waters has also been used as a prospecting tool for petroleum and natural gas

deposits or as a possible indicator of diagenetic processes accompanying petroleum formation (Kudel'skiy, 1977; Rittenhouse, 1967; and Valyashko, 1956).

There are few data on natural bromide and iodide levels in oil-field brines in Kansas, but iodide contents in the bordering Anadarko Basin have been examined by Collins (1969) and Collins and Egleson (1967). Leonard (1964) suggested that bromide and iodide levels could be used in evaluating oil-field brine pollution of the Walnut River in Kansas.

## Distribution of Bromine, Iodine, and Chlorine in the Lithosphere and Hydrosphere

Chlorine in igneous rock is present in three different modes, occurring either as a regular mineral constituent, as a replacement for hydroxyl groups in mineral structures, or as a constituent in inclusions. For bromide and iodide concentration the role of inclusions is believed to be significant, but replacement of chloride in mineral structures by bromide and iodide is the major mechanism by which these constituents occur in igneous rock (Correns, 1956). Selivanov (1940) calculated an average value of 314 ppm chloride and 1.62 ppm bromide for igneous rock, although Kuroda and Sandell (1953) determined average chloride to be lower, at 200 ppm. Goldschmidt (1958) estimated an average of 0.3 ppm iodide for magmatic rocks.

In most sedimentary rocks, chloride is low, and average concentrations decrease in order for carbonates (305 ppm), shales (170 ppm), and sandstones (5 ppm) (Hem, 1970). Values are appreciably higher for rocks with inclusions of connate brine. Mason (1966) reported 1.2-2.2 ppm iodide and 1-6 ppm bromide as average values for sedimentary rock. Higher concentrations occur for organic-bearing materials. Bennett and Manuel (1968) reported up to 50 ppm iodide in deep-sea sediments, and Price et al. (1970) reported up to 800 ppm iodide and 250 ppm bromide in surface sediments of the Barents Sea.

The concentration of iodide in anhydrite was determined by Roeber (1938) to range from 0.0155-0.1365 ppm. Bromide and iodide in salt occur by structure incorporation and in brine

inclusions. Raup (1966) determined that the bromide concentration in halite samples in the Paradox Basin, Utah, ranged from 65-270 ppm; Zak (1974) reported a concentration of 40-600 ppm for salts of marine origin in the Dead Sea. Holser (1966) interpreted low-bromide salts (25-60 ppm) to be second-cycle salts formed by second-cycle brines that have dissolved previously deposited salt strata.

Table 3 lists constituent values reported for waters from different sources. Fresh waters are generally low in bromide and iodide, although the I/Cl ratio of rainwater is approximately two orders of magnitude higher than that of seawater. Iodide concentration values reported for salt lakes of central Kazakhstan are also higher than those of seawater and are attributed by Mun and Bazilevich (1963) to the high sodium bicarbonate content of the waters. Bromide and iodide accumulate in interstitial waters in sediments, and both ions tend to increase with depth. The concentration of iodide in sediment, however, decreases with depth (Pavlova and Shiskina, 1973).

Oil-field brines may contain more than 200,000 mg/l chloride. Bromide is generally less than 50 mg/l, but may occur at concentrations up to 6000 mg/l. Iodide concentration generally is less than 10 mg/l, although it may commonly reach concentrations up to 100 mg/l (Collins, 1970). Brines of the Anadarko Basin containing up to 1400 mg/l are the highest recorded iodide contents for naturally occurring oil-field waters.

Table 3. Bromide, iodide, and chloride contents for selected waters, in mg/l.

	Br	I	Cl	Reference
Rain water	30-80µg/l	1-3µg/l	1	Winchester and Duce, 1965 Hem, 1970 Rankama and Sahama, 1950
River water	0.006	0.0018	8.3	Correns, 1956
Seawater	65	0.05	19,000	Rosler and Lange, 1972
Seawater, NaCl precipitation stage	4,000	5	275,000	Collins, 1975
Pore water, continental slope, northern Gulf of Mexico	60	-	22,000	Manheim and Bischoff, 1969
Salt lakes, central Kazakhstan	-	0.3-0.7	-	Mun and Bazilevich, 1963
Oil-field brines, Smackover Fm. Jurassic, Gulf Coast	3,126	25	171,686	Collins, 1974
Oil-field brines, Anadarko Basin, Pennsylvanian System	30-18,000	8-1,400	7,500-182,000	Collins, 1969

## Biogenic Factors Affecting Bromine and Iodine Concentration in Brines and Sediments

In seawater, iodine is present almost solely as iodate and iodide, with common marine redox equilibria predicting an iodate to iodide ratio of  $10^{13.5}$  at the pH and Eh of open ocean water (Sillén, 1961). Actual molar ratios range from as low as 1 in surface seawater to about 100 at ocean depths near 1000 m (Wong and Brewer, 1977). Ratios of iodate to iodide are generally much lower in fresh oxygenated water (Price and Calvert, 1977). Tsunogai and Sase (1969) attributed this speciation discrepancy to iodide production by iodate reduction carried out by nitrate-reducing bacteria. Enzyme studies using several bacteria strains determined that nitrate reductase used by aerobic bacteria in nitrate assimilation, proved to be an effective iodate-reducing agent. The iodide produced can be assimilated by other organisms or released to the atmosphere as free iodine.

Marine biota can concentrate appreciable amounts of bromide and iodide. The algae group is of prime importance in this capacity and utilizes only the iodide species (Baily and Kelly, 1955). Phaeophyceae (brown algae) and Rhodophyceae (red algae) are exceptionally iodide-rich; dried material of Laminaria digitata contains up to 17000 ppm iodide (Correns, 1956). Marine diatoms, characteristically a major contributor to sediment, contain as much as 30 ppm iodide in dried material (Correns, 1956). In addition, iodide accumulates in sponges, corals, mollusks, and the thyroid glands of marine vertebrate animals.



In comparison to marine organisms, non-marine flora and fauna do not concentrate substantial amounts of bromide or iodide.

The presence of organic matter in sediments is strongly correlated with bromide and iodide concentration, although the uptake sites for these halogens in organic matter are not known. Organic matter in natural waters is present predominantly in solution and as colloidal material in suspensions of organisms and detritus. Through photosynthesis, autotrophic plants are capable of converting inorganic to organic matter, with unicellular algae as primary converting reagents. The major portion of the plankton biomass is within the upper 100 m of water (Bordovskiiy, 1965), and the organic matter is carried to greater depths by active vertical migration of feeding organisms. Suspended particles such as clays then absorb organic materials from water and incorporate them into sediments. Pavlova and Shiskina (1973) indicated that factors, such as sediment type, rate of sedimentation, and other chemical and physical parameters may play a role in determining the concentration in sediment of iodide and bromide.

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## GEOLOGY

### Oil-field Brines

Petroleum reservoirs in Kansas occur in all Paleozoic systems and in some fissured quartzitic Precambrian rocks. The dolomite of the Arbuckle Group (Ordovician) and the associated basal Reagan Sandstone (Lamotte Sandstone) lead in cumulative production, with nearly half of Kansas-produced oil designated as Arbuckle (Landes, 1970). The basal Pennsylvanian sandstone strata rank second in production importance as reservoirs, followed by Mississippian limestone reservoirs, and the Viola Limestone and Simpson Group of the Ordovician System. Figure 3 is a geologic column of petroleum and natural gas reservoir rocks in Kansas.

Large quantities of brine commonly are produced with oil. Disposal practices of the past included spreading waste brine on fields and roads or emptying it into ditches and streams. Groundwater contamination also arose from wells that were not adequately cased or from abandoned wells that were not properly plugged, and from infiltration from disposal ponds. Incidents of brine pollution still occasionally occur from accidental or illegal spills and from uncased or poorly cased wells, especially in areas of waterflooding.

System	Stage	Series	Thickness, feet	Designation
			5000	Overlying rocks (Upper Permian redbeds and evaporites, Cretaceous and Tertiary strata)
Permian	Lower	Gearyan	335	Chase Group (Gas Reservoirs)
			320	Council Grove Group (Gas Reservoirs)
			130	Admire Group
Pennsylvanian	Upper	Virginian	500	Wabaunsee Group
			325	Shawnee Group
			340	Douglas Group
	Upper	Missourian	430	Lansing-Kansas City Groups
			100	Pleasanton Group
	Lower Middle	Desmoinesian	250	Marmaton Group
			450	Cherokee Group
			30	Basal Pennsylvanian deposits
Mississippian	Lower to Upper		650	"Chat" and "Mississippi Lime" (undifferentiated)
Devonian	??-??-??-??-??-??-??		150	Chattanooga Shale
Silurian			200	"Hunton Group"
Ordovician	Lower Middle Upper			////////////////////////////////////
			40	Maquoketa Shale
			160	Viola Limestone
			90	Simpson Group
Cambrian			600	Arbuckle Group
				Reagan or Lamotte Sandstone

Figure 3. Petroleum reservoir rocks in Kansas  
(from Landes, 1970 and Zeller, 1968).

## Petroleum Reservoirs of Russell County

A series of reservoir carbonates exist in present-day Russell County, as a result of regional marine inundation throughout Pennsylvanian time and conditions that allowed for petroleum production and accumulation. Many petroleum structural traps were produced by Late Mississippian-Early Pennsylvanian tectonic activity associated with the Central Kansas Uplift. The oldest reservoir rocks in the uplift area, the Arbuckle Group, consist of five divisions of Cambro-Ordovician cherty limestone and dolomite and unconformably overlie the Precambrian basement. The "Gorham sand" is a local designation for a cherty basal Pennsylvanian deposit that is identified by Merriam (1963) as Mississippian-deposited material later reworked by Pennsylvanian seas.

Limestone strata of the Pennsylvanian Lansing Group are highly productive in many places and are produced jointly with the Kansas City Group. The Wabaunsee Group consists primarily of shale but includes some interbedded limestone, e.g. the Tarkio Limestone, and lenticular sandstone that belongs to the Upper Pennsylvanian Series.

A small amount of water from the Cedar Hills Sandstone is included in the Kuhnle Smoky Waterflood Unit. The Cedar Hills is defined as approximately 180 ft of red sandstone interbedded with softer shaley red siltstone lying above the Permian Salt Plain Formation (Norton, 1939). The term, Cedar Hills Sandstone, is also used loosely to define sandstone strata near this horizon. In the past, the high permeability of the formation made it a desirable shallow zone for disposal of brines.

Brine samples from Russell County were collected from several producing zones, ranging from the Arbuckle Group of the Upper Cambrian and Lower Ordovician series to the Tarkio Limestone Member of the Upper Pennsylvanian Series. The Kuhnle Smoky Waterflood Unit had formerly received an input of water from the Cedar Hills Sandstone of the Lower Permian Series, but the pumping had been discontinued. The water contributed from this source composed less than five percent of the waterflood-unit brine.

### Petroleum Reservoirs of Butler County

The El Dorado Field in Butler County was discovered in 1914 and became an early major development area for the Kansas petroleum industry. Oil-bearing structures are associated with the southern extension of the Nemaha Anticline. Major zones currently producing oil in the El Dorado Field are the Pennsylvanian Lansing-Kansas City groups, the Mississippian System, the Siluro-Devonian Hunton Group, the Ordovician Viola Limestone and Simpson Group, and the Cambro-Ordovician Arbuckle Group. Brines associated with the Kansas City, Viola, and Arbuckle were collected in Butler County.

The Kansas City Group belongs to the Missourian Stage (Upper Pennsylvanian Series) and conformably overlies the Pleasanton Group. The Kansas City Group is overlain by the Lansing which thickens regionally to approximately 250 ft. Consisting of alternating marine and non-marine units, the Kansas City Group consists of twelve formations and in Butler County ranges in thickness from approximately 125 to 200 ft (Merriam, 1963).

In the subsurface in the northern half of Butler County, the Viola Limestone (Middle Ordovician) overlies the Middle Ordovician Simpson Group. In the Oil Hill dome region, the Viola Limestone underlies Pennsylvanian rocks (Landes, 1970). Lee (1943) described the Viola Limestone as a medium-to-coarse crystalline dolomite with varied amounts of chert.

### Petroleum Reservoirs of Ness County

Brines were obtained from lenticular sandstone reservoirs in the Lower Pennsylvanian Cherokee Group. These beds are generally 8 to 10 ft thick and are separated from the underlying Mississippian by varied amounts (25 to 75 ft) of shale. The sandstone beds probably constitute a portion of ancient deltaic deposits (Walters et al., 1979). The Central Kansas Uplift was an active tectonic feature during the Early Pennsylvanian Epoch. As the sea advanced northward, materials from this positive feature were reworked and distributed in adjacent basins. Cherokee Group beds in Ness County abut against the Central Kansas Uplift. Eight oil-field water samples were collected at the wellhead.



### Brines Associated with Permian Salt

Permian salt beds in Kansas are primarily in the Blaine, Stone Corral, and Wellington formations in the Middle Permian Series. The Wellington Formation and the overlying Ninnescah Shale, together with the Stone Corral Formation constitute the Sumner Group.

The Wellington Formation in the subsurface generally consists of an upper layer of gray shale, a rock-salt member, and lower deposits of anhydrite with some interbeds of dolomite. The Hutchinson Salt Member of the Wellington Formation occurs in the subsurface over a large area of Kansas and parts of Oklahoma and the Texas Panhandle. In Kansas, the maximum thickness exceeds 700 ft. The depth of the western margin of the Hutchinson Salt in many areas is sufficient to prevent solution by groundwater, but the eastern margin is, in many areas, within 200 ft of the surface and prone to dissolution. Traces of an unconformity at the top of the Hutchinson strongly indicate that the original margin of salt deposition extended farther eastward. Dellwig (1963) suggested that salt removed from an earlier eastern margin may have provided source material to the upper part of the Hutchinson Salt. The absence of dissolution within the body of the deposit is credited to the capping by Permian red beds and impermeable shale (Walters, 1976).

The Hutchinson Salt Member is stratigraphically complex, with interbeds of clay and anhydrite occurring throughout and with varied thickness. A shallow depositional basin is indicated by features such as mudcracks and ripple marks in clay laminae.

Periodic inflow of fresh water is suggested by the clay layering, but no cyclic pattern is evident. The absence of deformation indicates the salt beds have not been subjected to significant tectonic activity since deposition. Mapped sections do indicate slight thinning of salt beds over major oil fields.

Brines from Salt-Solution Mining, Reno County.--The bedded salt of the Hutchinson Salt Member near Hutchinson, Kansas is 325 ft thick; the top of the salt bed occurs at a depth of approximately 400 ft. Clay and anhydrite are impurities and occur as irregularly spaced "Jahresringe" laminae and as thick beds. Shale occurs in discontinuous layers and lenses suggestive of shallow-water deposition. The smooth contacts of these shales with underlying salt suggests that fresh waters depositing clay materials also had opportunity to erode the salt surface (Dellwig, 1963). Veins of red salt are abundant in shale layers; ferric iron residue is the source of pigmentation. Whereas shale deposits provide evidence of fresh-water inflow to the basin, beds and laminae of anhydrite indicate periodic addition of brines (Dellwig, 1963).

The member is characterized by layering of clear and cloudy salt, and varied halite crystal sizes. Large crystals are generally clear, whereas smaller ones characteristically contain fluid inclusions outlining pyramidal hopper crystals. Kulstad (1959) provided a detailed account of the occurrence of the Hutchinson Salt in Kansas.

The dissolved halite core sample obtained from a Lyons mine in Rice County is also a portion of the Hutchinson Salt

Member. Salt beds in this region occur at a depth of 1000 ft and also are stratigraphically complex. The Wellington Formation is overlain by approximately 290 ft of Ninnescah Shale in Rice County (Norton, 1939).

Brines from the Smoky Hill River Valley, Saline County.--  
The Smoky Hill River valley contains sediments of Tertiary to Recent age, underlain in parts of Saline County by Cretaceous and Permian rocks. Locally, the Wellington Formation reaches a thickness of 700 ft and consists primarily of gray shale with lenses of limestone and gypsum. Where undissolved, the Hutchinson Salt Member occurs in the subsurface near midformation.

The Kiowa Formation (Lower Cretaceous Series), composed of shale, clay, and lenticular beds of iron-rich sandstone, attains a maximum thickness of 200 ft in the valley (Latta, 1949), and with exception of the sandstone beds, is a poor water source.

Permian rocks underlie alluvium of Pleistocene to Recent age in the vicinity of the town of Solomon. The range of thickness of alluvium is 30-90 ft (Latta, 1949), and the stream-deposited materials consist of clay, silt, sand, and gravel. Numerous springs and seeps of varied salinity are found along the Smoky Hill and Solomon rivers. As it is throughout most of the Smoky Hill valley, the alluvium is a major source of water for the Solomon area; depth to the water table is 20-30 ft.

Waters from the Dakota Formation, Russell County

The water-bearing formations in Russell County include the Cretaceous to the Quaternary systems, with Cretaceous rocks

generally dipping westward. In the vicinity of the city of Russell, thin layers of silt, sand, and gravel of the Quaternary System overlie the Carlile Shale of the Upper Cretaceous Series. To the north and south of Russell, the Saline and Smoky Hill rivers cut deeply into older rocks. The river valleys contain Recent and Pleistocene alluvial deposits, and the Greenhorn Limestone, the Graneros Shale, and the Dakota Formation in the Upper Cretaceous Series are exposed in valley walls.

The Dakota Formation is the oldest rock exposed in the vicinity. Latta (1948) reported that approximately 160 ft of Dakota sandy shale and sandstone have been exposed through erosion of the Smoky Hill and Saline rivers. Regionally, the Dakota Formation lies between the Kiowa Formation and the Graneros Shale. The Dakota consists of continental and littoral deposits indicative of coastal lagoon and tidal marsh environments (Frye and Brazil, 1943). Channel sandstone is common but discontinuous. The Dakota sandstone strata yield moderate water supplies, characteristically sufficient for domestic and stock wells in parts of central and western Kansas. Many water-yielding zones, however, contain waters too highly mineralized for domestic or agricultural use.

## METHODS OF INVESTIGATION

### Sample Collection

All samples were collected and stored in polyethylene containers. Company representatives assisted in collecting oil-field brines. Taps from wellheads and brine tanks were allowed to flow briefly in order to clear lines and to provide representative samples. Two liters of each brine were collected.

Ness County oil-field waters were sampled in September, 1977. All were taken from the wellhead. Because of generally low ratios of water to oil, a separation was performed in the field; upon gravity settling the brine was drained and gathered into another container. Russell County samples were collected in February, 1978. Brine separators and a waterflood unit containing mixtures of brines were sampled, together with water from some wellhead taps. The proportion of each contributing brine source as approximated by the field representative, was recorded. The El Dorado area of Butler County was sampled in April, 1978. All samples were untreated brines from separators, and one water was a product of secondary recovery operations.

A representative of Carey Salt, Division of Interpace Corporation was requested to collect brine samples at the Hutchinson mining operation in May, 1978. The brines were taken from solution mining wellheads before the waters could be pumped into settling tanks.

The wells sampled in Saline County in June, 1978, are maintained by the Kansas Water Office in Topeka. Because fresh water had been added to the well to maintain water levels, each well was hand-bailed until saline waters were withdrawn from the aquifer.

Salt Creek samples were gathered in July, 1978. Along a half-mile traverse of the stream, specific conductivities were measured using a portable Wheatstone-bridge meter and conductivity cell. Water temperatures were also recorded. A progressive increase in conductivity was recorded while travelling west of the Canyon Road bridge (Fig. 2), and a sharp increase was found downstream east of the same bridge, indicating two probable salt seeps along the course. Grab samples were obtained from the middle of the stream.

### Sample Preparation

All waters were filtered in the laboratory through 0.45  $\mu$ m membrane filter papers within twelve hours after field collection. Oil-field waters which contained oil droplets and other substantial impurities were initially filtered through a series of coarser grade papers. For cation determination, 250 ml of each filtered sample was acidified to pH 3 with reagent grade concentrated nitric acid. Oil-field brines were allowed to gravity settle overnight before filtration, and brines with overlying thick oil layers were drawn out by pipetting.

Brine from a core segment of Hutchinson Salt was prepared by weighing the halite sample and dissolving it in a known volume of distilled and deionized water. The brine was filtered to remove small amounts of fine-grained insoluble residue associated with the halite. Constituents were then determined as with other samples.

### Analytical Methods

All chemicals used in constituent determinations were reagent grade and distilled and deionized water was used in preparation of all reagents, standards, and dilutions. Sulphate was determined within seven days of collection, using the turbidimetric method of Brown et al. (1970), wherein sulphate ion forms a colloidal suspension upon addition of barium chloride in salt-acid glycerol medium. Percent transmittance against a deionized water blank was determined photometrically in a Coleman Model 14 Universal Spectrophotometer. Sulphate concentration was then obtained using a calibration curve prepared from analyses of standards.

Determination of chloride was performed by argentometric titration (Taras et al., 1971). A sample aliquot containing potassium chromate indicator was titrated with standardized silver nitrate solution. The endpoint occurred upon appearance of red silver chromate precipitate, indicating a slight excess of silver. Oil-field brines containing high amounts of interfering sulfide were pretreated by acidification with sulfuric acid, followed by addition of 15 percent hydrogen peroxide (Collins, 1975) and gentle heating. The pH was adjusted to neutral or slightly alkaline with sodium hydroxide solution.

Bromide was determined by hypochlorite oxidation (Brown et al., 1970). Bromide and iodide are collectively oxidized by hypochlorite, and sodium formate is used to reduce any excess hypochlorite. Upon addition of potassium iodide in acidic conditions, iodine is liberated in amounts equivalent to bromate



and iodate collectively, and iodine can be titrated with standardized sodium thiosulphate and starch indicator. Samples were pretreated for interferences of iron, manganese, and organic substances by addition of calcium oxide followed by filtration. Oil-field brines were allowed to stand overnight with calcium oxide. Iodide was determined on a separate aliquot, and the difference was calculated as bromide.

In addition, bromide was determined by X-ray fluorescence as described by Dunton (1968); the ratio of the intensity of bromine K-alpha radiation and the background intensity is measured using fixed-time operation. Concentration was obtained from a standard curve. Because of the scarcity of other oxidation states for bromine in most brines, this analytical method is suitable in bromide determination.

A titrimetric method was used for iodide determination in samples where concentrations exceeded 1 mg/l (Brown et al., 1970). Calcium oxide treatment, as in the hypochlorite oxidation method, was required to remove interferences. Bromine oxidizes iodide to iodate in the presence of sodium acetate solution and acetic acid, and sodium formate is used to decompose any excess bromine. Liberated iodine from the addition of potassium iodide is titrated with standardized sodium thiosulfate.

Waters whose iodide contents were anticipated as less than 1 mg/l were analyzed by ceric-arsenious oxidation used by Brown et al. (1970). During the ceric-arsenious oxidation reaction in acid, iodide behaves catalytically, and the extent of the reduction of ceric ions, under given reaction time and

temperature conditions, is in proportion to iodide concentration. Samples and standards were diluted and acidified with sulfuric acid, then treated with arsenious acid. A constant-temperature bath kept solutions  $30 \pm 0.5^\circ\text{C}$ . Upon incubation, ceric sulphate solution was added at reaction onset. Addition of silver ion (silver nitrate solution) stopped the reaction, and the extent of the process was determined by measuring sample absorbance in the spectrophotometer and by calculating sample concentrations from a standard curve.

Some samples were also analyzed for iodide using an Orion Model 94-53 specific-ion electrode. This measurement was not suitable for waters with very low iodide to chloride ratios. The method of known addition as recommended by the manufacturer was employed for those samples measured.

Calcium, magnesium, sodium, and potassium were determined by atomic absorption using an air-acetylene flame and hollow cathode lamps and a Perkin-Elmer Model 305 B Atomic Absorption Spectrophotometer. One percent by weight of lanthanum was added to samples and standards analyzed for calcium, to overcome the effects of sulphate and several other constituents commonly present in water, that depress sensitivity. Lanthanum also compensates the slight ionization of calcium by air-acetylene flame. Sodium and potassium are partially ionized in an air-acetylene flame; excess sodium (2000 mg/l) was added to sample aliquots analyzed for potassium: excess potassium was added to those samples used in sodium determinations. The analyses of calcium, magnesium, sodium, and potassium were checked by

inductively coupled argon plasma spectrometry (Jarrell Ash Model 975 Plasma Autocomp) at the Kansas Geological Survey. Strontium and lithium were also determined using this instrument; analyses were performed by T. Waugh at the Kansas Geological Survey.

## RESULTS AND DISCUSSION

### Oil-field Brines

Concentrations of chemical constituents for Ness, Russell, and Butler counties oil-field waters are given in Tables 4 and 5. The area and range of depth from which the Ness County brines were sampled are relatively confined, and the brines exhibit great chemical similarity. Brines from Russell and Butler counties were collected from more diverse areas and producing horizons and show greater variation. In the area sampled in Russell County, the overlying "Gorham sands" is frequently associated with the Arbuckle Group, and brines sampled from these two producing zones (sample numbers 0 10 R and 0 11 R, respectively) were chemically similar.

The chloride concentration for most brines was greater than that of seawater, which averages 19,000 mg/l chloride. Table 6 lists concentrations for chloride and other constituents for seawater and evaporating seawater. The waters produced from the Viola Limestone in Butler County and from the Middle Pennsylvanian-Mississippian strata in Ness County contained chloride amounts equal to or lower than that of seawater. The regional mechanisms controlling ion mobility cannot be determined in this study; however, man-made causes of dilution such as fresh-water introduction are not known to exist locally.



Table 4. Cation analyses of oil-field brines. (Continued)

Well or Field	Sample Number	Ca	Mg	Na	K	Sr	Li
		-----mg/l-----					-----
		Butler County					
ElDorado 25-5-5 <sup>a</sup>	017B	4000	1630	34100	150	---	4.8
ElDorado 25-5-30	018B	1000	310	7240	110	51	4.2
ElDorado 25-5-21	019B	2100	710	15400	130	470	4.8

<sup>a</sup>Township, range, section.

Table 5. Anion analyses of oil-field brines.

Sample Number	SO <sub>4</sub>	Cl (mg/l)	Br	I
Ness County				
01N	1835	18900	30	1.2
02N	1900	18000	18	1.2
03N	2000	18000	18	1.1
04N	1880	17900	9	1.0
05N	1560	18800	22	1.0
06N	2040	17900	18	1.0
07N	1910	18000	16	1.0
08N	--	18200	17	1.1
Russell County				
010R	1000	36700	98	3.7
011R	1200	36500	98	3.8
012R	1400	59500	170	7.9
013R	100	25500	87	3.6
014R	400	60900	180	9.6
Butler County				
017B	400	66400	220	9.8
018B	1800	13100	13	1.9
019B	2000	29300	72	4.2

Table 6. Average composition of seawater and changes in concentration with evaporation. Values in mg/l.

Constituent	Seawater	Precipitation stage				
		CaSO <sub>4</sub>	NaCl	MgSO <sub>4</sub>	KCl	MgCl <sub>2</sub>
Calcium	400	1700	100	10	0	0
Magnesium	1300	13000	74000	80000	130000	153000
Sodium	11000	98000	140000	70000	13000	12000
Potassium	350	3600	23000	37000	26000	1200
Lithium	0.2	2	11	12	27	34
Strontium	7	60	10	1	0	0
Chloride	19000	178000	275000	277000	360000	425000
Bromide	65	600	4000	4300	86000	10000
Iodide	0.05	2	5	7	8	8

Adapted from Table 7.III Collins (1975)



Bromide and iodide values ranged widely, from 9-220 mg/l bromide and 1.0-9.8 mg/l iodide. Oil-field brines sampled in a study of Stafford County (Whittemore and Pollock, 1979) contained up to 19.4 mg/l iodide. Some waters, particularly in Ness County, were depleted in bromide relative to the 65 mg/l content of seawater, but all study brines were enriched in iodide compared to seawater (0.06 mg/l).

Lithium, the lightest of alkali elements and commonly enriched in oil-field waters, ranged from 4.2 to 15.1 mg/l; all values exceeded seawater content of 0.2 mg/l. Although most brines contain less than 10 mg/l, Collins (1978) described oil-field brines from the Smackover Formation that contain up to 692 mg/l. The data in Table 6 indicate that lithium in brines produced by late-stage seawater evaporation is significantly lower than this value.

The concentration of the major cations sodium and magnesium ranges both above and below seawater concentrations. In all samples, calcium was enriched and potassium depleted in comparison with average seawater contents of 400 mg/l and 350 mg/l (Table 6), respectively. Ratios of potassium to chloride for the Ness County samples are only slightly lower than K/Cl for seawater (0.018), but these ratios for all other brines indicate that potassium was adsorbed by associated minerals of the surrounding rock.

Table 7 lists ranges and medians of some chemical constituents as determined by other studies conducted on the same producing horizons within the counties examined in this study.

Table 7. Ranges and medians for major chemical constituents in oil-field brines from producing zones and counties examined in this study. Data from other studies<sup>a</sup>.

Producing Zone	Number of Samples	Range (mg/l)				Median (mg/l)						
		Na	Ca	Mg	SO <sub>4</sub>	Cl	Na	Ca	Mg	SO <sub>4</sub>	Cl	
		Ness County										
Cherokee Group	4	--	1560- 3430	300- 790	---	25200- 40000	--	2050	470	---	24600	
Mississippian System	7	--	640- 2000	300- 450	---	10200- 19600	--	1660	380	---	17100	
		Russell County										
Gorham Sands	4	6590- 20700	970- 2060	290- 970	1390- 2640	11450- 36400	11300	1620	530	2130	20000	
Arbuckle Group	85	--	790- 3820	390- 1460	400- 4300	17600- 41800	--	2320	590	2490	21300	
Lansing Group	65	--	1000- 24800	560- 8660	0- 2800	13500- 118000	--	7500	2140	1390	64100	
Wabaunsee Group (Tarkio Limestone Member)	22	--	500- 12800	300- 3450	150- 6000	21700- 116400	--	8550	2380	880	87400	
		Butler County										
Arbuckle Group	7	--	1380- 2780	210- 560	200- 2260	14700- 24800	--	1800	500	1380	18900	

<sup>a</sup>Kansas Geological Survey, Computer Listing.

The determinations were compiled at the Kansas Geological Survey and were performed mostly in the late 1950's to middle 1960's, with some additional results reported in the 1970's. Constituent values from Tables 4 and 5 generally fit well into the ranges shown on Table 7. Constituent data for formation waters have been used in mapping distributions of dissolved solids, and these distributions have been applied in petroleum exploration of areally extensive formations. For example, a chloride map of Arbuckle - associated waters covering Kansas and Oklahoma and contoured using 20,000 mg/l chloride intervals was prepared by Chenoweth (1964). Although restricted by producing zone and county, the values for brines sampled in this study show wide diversity for all major cations examined and overlap of values among producing zones. Likewise, ratios of values, e.g. Ca/Cl, Ca/Mg, Ca/SO<sub>4</sub>, and Mg/SO<sub>4</sub>, fail to distinguish producing zones on this areal scale. Diversity within the producing horizon of some of the dissolved solids, and especially salinity, may be attributed to local variations of factors such as hydraulic gradients, soluble material in the associated rocks, and clay membrane filtration. Although the use of certain major constituents may be applicable in some areas for formation water identification, the counties and producing zones examined in this study were not investigated in sufficient detail to attempt similar observations, inasmuch as more thorough investigation of local geology would be required.

Constituent ratios for each sample are listed in Table 8. Table 9 gives ranges of ratios for the sampled producing horizons.

Table 8. Weight ratios of chemical constituents for oil-field brines.

Sample Number	Na/Cl	Br/Cl $\times 10^4$	I/Cl $\times 10^6$	Li/Cl $\times 10^5$	Sr/Cl $\times 10^3$	Br/SO <sub>4</sub> $\times 10^2$	I/SO <sub>4</sub> $\times 10^3$	Br/I
Ness County								
01N	0.55	16	63	77	2.80	---	---	25
02N	0.54	10	67	76	2.90	---	---	15
03N	0.53	10	61	81	2.90	---	---	16
04N	0.53	5.0	56	78	2.90	---	---	9
05N	0.55	12	53	70	2.90	---	---	22
06N	0.54	10	56	77	2.90	---	---	18
07N	0.53	8.9	56	84	2.90	---	---	16
08N	0.55	9.3	60	75	2.70	---	---	15
Russell County								
010R	0.48	27	100	18	7.10	8.2	3.7	26
011R	0.47	27	100	19	5.50	9.8	3.2	26
012R	0.48	29	130	9.8	4.00	12	5.6	22
013R	0.47	34	140	8.8	5.90	87	36	24
014R	0.48	30	150	7.6	7.10	45	24	19
Butler County								
017B	0.51	33	150	7.2	---	55	24	22
018B	0.55	10	140	32	3.40	7.2	1.0	6.8
019B	0.52	25	140	16	16	3.6	2.1	17

Table 9. Ranges of weight ratios of constituents for oil-field brines, according to producing horizon.

Producing Zone	Number of Samples	Na/Cl	Br/Cl $\times 10^4$	I/Cl $\times 10^6$	Li/Cl $\times 10^5$	Sr/Cl $\times 10^3$	Br/I
Tarkio Lansing	2	0.47-0.48	29-34	130-140	8.8-9.8	4.0-5.9	22-24
Lansing- Kansas City	2	0.48-0.51	30-33	150	7.2-7.6	7.1	19-22
Cherokee	5	0.53-0.55	24-30	66-77	84-98	2.7-2.9	35-46
Gorham (basal Pennsylvanian)	1	0.48	35	98	18	7.1	35
Ft. Scott- Mississippian	3	0.53-0.54	6.4-29	63-81	35-89	2.9	7.9-40
Viola	1	0.51	33	150	7.2	---	22
Arbuckle	2	0.47-0.52	25-27	100-140	16-19	5.5-16	17-26

The Na/Cl ratio for Ness County waters is similar to that of seawater (0.556). The Na/Cl ratios for Russell County are slightly lower and may possibly be the result of sodium depletion by diagenetic processes of ion exchange.

Less variability occurs in I/Cl ratios than Br/Cl and Br/I ratios. The more saline brines of Russell and Butler counties have higher Br/Cl and I/Cl ratios than the Ness County samples. Both Li/Cl and Sr/Cl ratios show strong enrichment relative to values anticipated during seawater evaporation. Seawater Li/Cl ratio has a value of  $1.05 \times 10^{-5}$ , and lithium does not diminish as evaporation occurs. A general trend observed for samples in this study is that high-lithium waters had lower strontium. In a study of Smackover Formation brines, potassium depletion was shown to have been associated with lithium enrichment (Collins, 1978). Potassium readily replaces lithium in lattices of associated clays, thereby releasing lithium into solution. All samples had lower K/Li ratios than seawater (1750). During evaporation, K/Li ratios increase until potassium chloride precipitates. Because oil-field brines are not generally believed to experience such late-state evaporation, potassium depletion relative to lithium indicates an ion-exchange process.

Ratios of  $\text{Br}/\text{SO}_4$  and  $\text{I}/\text{SO}_4$  were highly varied. With one exception, low sulphate waters are associated with those samples containing high calcium, magnesium, and sodium, a characteristic common to oil-field waters. Although bromide and iodide do not participate in mineralization reactions in brines, chemical reactions involving sulphate in brine are controlled by two

common processes: bacterial reduction of sulphate to hydrogen sulfide together with dolomitization of reservoir rock result in low-sulfate waters. During dolomitization, magnesium, in reacting with calcium carbonate, releases calcium into solution, thus allowing in some instances sulphate precipitation as gypsum.

The ranges and medians for bromide and iodide in brines of different producing zones, as determined by values from other studies in Kansas, are compared in Table 10. Arbuckle Group brines contain lower iodide and especially lower bromide concentrations, compared with other median values. A wide range of bromide contents is found in all producing zones examined, with concentrations in some instances less than the Br/Cl ratio for seawater at that particular chloride concentration. Fresh-water dilution or mixing with other water sources cannot be ruled out as a possible cause in these instances. Iodide values vary in a narrower range, and all ratios to chloride exceed that of seawater. None of the samples typifies some of the very high iodide brines of the neighboring Oklahoma Anadarko Basin.

Comparison of weight ratios of minor constituents to chloride among producing zones in Kansas shows much overlap of ranges. No progressive trends are observed with different horizon ages. Inasmuch as constituent distribution is controlled by several variables, among them solution of evaporite minerals, dilution, leaching, and ion filtration through clay membranes, a more detailed examination of a small study area may permit classification of a water, using constituent ratios, by local producing zone.

Table 10. Range and median for bromide and iodide in several producing horizons in Kansas. Other studies<sup>a</sup>. Results given in mg/l.

Producing Horizon	Number of Samples		Range		Median	
	Br	I	Br	I	Br	I
Lansing-Kansas City Groups	15	18	10-315	2-20	140	10.6
"Chat" (Mississippian System)	12	12	10-325	6-12	160	5.4
Mississippian System	3	3	26-370	7-23	190	11.0
Viola Limestone	7	5	9-460	1-7	120	6.2
Arbuckle Group	22	22	26-138	<1-12	56	2.8

<sup>a</sup>Data from several sources: Kansas Geological Survey Computer Listing, Collins (1969), and Schoewe (1943).



### Halite-Solution Brines and Saline-Formation Waters

Concentrations of chemical constituents determined for saline waters of other than oil-field source are listed in Tables 11 and 12. All samples are sodium chloride waters with minor amounts of calcium, magnesium, and sulphate, and smaller quantities of additional constituents. Waters from Salt Creek are placed in this category as representative of waters in which salinity is contributed by formation waters.

Solution brines from salt mining at Hutchinson, Kansas were the densest brines sampled. Salt mined in the region generally contains calcium sulphate as the major impurity, composing up to four percent by weight of rock salt according to analyses released by Carey Salt Company. Sample number H 23 E, also a halite solution, was prepared by dissolving a portion of a halite core in deionized water. Differences in composition between this sample and the Carey solution brines can be attributed to variations within the Permian salt beds together with effects possibly caused by well waters from local aquifers used in the solution-mining operation.

Calcium contents of the samples from observation wells in Saline County indicate that there has been dissolution of some associated calcium sulphate minerals. Waters from Salt Creek in Russell County do not indicate dissolution of sulphate evaporities but differ from other samples by high magnesium in relation to calcium. The Mg/Ca ratio for these samples increases for the more saline waters. The waters are also more enriched in potassium.

Table 11. Cation analyses of halite-solution waters and formation waters.

Identification or location	Sample Number	Ca	Mg	Na	K	Sr	Li ( $\mu\text{g/l}$ )
		-----	-----	(mg/l)-----	-----	-----	
Halite-Solution Waters							
Carey #82	H15Re	1730	670	121000	110	26	910
Carey #98	H16Re	1720	920	117000	140	25	1380
Lyons Salt core	H23E	127	3.3	9940	<1	1.6	65
Observation Wells, Saline County							
SW.1/4NE.1/4SW.1/4, Sec. 14, T.13S., R.1W.	H20S	890	130	10800	7.1	16	300
SE.1/4SW.1/4SE.1/4, Sec. 35, T.13S., R.1W.	H21S	1240	380	33600	25	25	560
NW.1/4SW.1/4SW.1/4, Sec. 32, T.13S., R.1W.	H22S	1560	450	38400	26	29	630
Salt Creek, Russell County							
SE.1/4NW.1/4SE.1/4, Sec. 6, T.13S., R.14W.	F24R	123	195	3940	20	0.4	980
NE.1/4NE.1/4SE.1/4, Sec. 6, T.13S., R.14W.	F25R	124	103	1970	13	0.3	490
SE.1/4SE.1/4SW.1/4, Sec. 6, T.13S., R.14W.	F26R	124	210	4180	21	0.4	1130
NW.1/4SE.1/4SW.1/4, Sec. 6, T.13S., R.14W.	F27R	183	420	8420	28	0.7	2270

Table 12. Anion analyses of halite-solution waters and formation waters.

Sample Number	SO <sub>4</sub> -----	Cl (mg/l) -----	Br -----	I (µg/l)
Halite-Solution Waters				
H15Re	3600	186000	57	1100
H16Re	3900	182000	74	1100
H23E	--	15300	1.6	15
Observation Wells, Saline County				
H20S	1900	16700	2.6	180
H21S	3800	53600	9.0	200
H22S	3700	61200	10	220
Salt Creek, Russell County				
F24R	1600	5760	1.8	50
F25R	1000	2960	1.0	30
F26R	1600	6030	2.0	40
F27R	2600	12400	4.2	90

Since bromide tends to remain in solution during crystallization of halite, only a small portion of the bromide available in the parent brine replaces chloride in the halite-crystal structure, resulting in very low bromide for halite-solution waters. Iodide concentrations in salt also are controlled by a similar process. These observations apply to samples of this study.

Values for weight ratios of halite-solution brines and formation waters are given in Table 13. All waters had high values of the Na/Cl ratios; many were as high as pure halite (0.649). The waters gathered at Salt Creek slightly exceed this value. Ratios of Br/Cl, I/Cl, and Li/Cl for Salt Creek waters were also higher than for those ratios for halite-solution waters. Among the observation wells of Saline County, sample number H 20 S had significantly lower chloride and some differences in weight ratios, such as higher I/Cl, Li/Cl, and I/SO<sub>4</sub> but a similar ratio of Br/Cl and a lower ratio of Sr/Cl. Lithium and iodide appear to be enriched by the dilution of chloride upon mixing of fresh water. The ratio Br/I varies greatly among samples, probably reflecting differences in the chemical behavior of bromide and iodide within an environment. For example, mechanisms such as leaching or absorption by organic material may have affected these constituents differently.

As bromide content in halite is determined by the respective parent brine, repeated solution and reprecipitation of the halite in situ during deposition contributes to the lowering of bromide concentrations in the later salts. Holdoway (1978) reported 5-20 ppm bromide for salt in the Blaine Formation of the

Table 13. Weight ratios of constituents for saline waters of other than oil-field source.

Sample Number	Na/Cl	Br/Cl $\times 10^4$	I/Cl $\times 10^6$	Li/Cl $\times 10^5$	Sr/Cl $\times 10^4$	Br/SO <sub>4</sub> $\times 10^3$	I/SO <sub>4</sub> $\times 10^5$	Br/I
Halite-Solution Waters								
H15Re	0.649	3.1	5.9	0.49	1.4	16	30	52
H16Re	0.643	4.1	6.0	0.76	1.4	19	28	67
H23E	0.650	1.0	1.0	0.42	1.0	--	--	110
Observation Wells, Saline County								
H20S	0.645	1.6	11	1.8	0.96	1.4	9.5	13
H21S	0.626	1.7	3.7	1.0	4.7	2.4	5.2	14
H22S	0.627	1.6	3.6	1.0	4.7	2.7	5.9	45
Salt Creek, Russell County								
F24R	0.683	3.1	8.7	17	0.69	1.1	3.1	36
F25R	0.668	3.4	10	17	1.0	1.0	3.0	33
F26R	0.693	3.3	6.6	19	0.66	1.2	2.5	50
F27R	0.680	3.4	7.3	18	0.56	1.6	3.4	47

Nipewella Group: he attributed the values to redissolution followed by reprecipitation of salt beds. The salt material for both the Hutchinson Salt Member of the Wellington Formation and the Lyons core sample contains higher original bromide, more typical of a marine evaporated salt (approximately 100 ppm and 35 ppm for Hutchinson and Lyons samples, respectively).

The Br/Cl ratio of Salt Creek waters is approximately ten times lower than that of seawater. The formation brines in the Dakota Formation may have dissolved halite crystals originally deposited in the strata. If they are connate waters assumed to be ancient seawater, diagenetic processes occurring during lithification of the sediments must account for bromide depletion. As another alternative, the original source for the present intraformational water might have been from solution of evaporites in underlying units; these waters may have then migrated along structural zones of greater permeability.

With exception of Salt Creek samples, all non-oil-field samples had Li/Cl ratios similar to or lower than that of seawater. Carpenter and Miller (1969) reported subsurface waters in Saline County, Missouri containing lithium enriched twenty times relative to seawater; they suggested that rock material - water interactions were responsible for this enrichment. Upon release during rock weathering, lithium tends to remain in solution. Lithium in some evaporities is enriched, as in the Clayton Valley brines of Nevada, where Kunasz (1974) reported lithium concentrations of 38 mg/l for springs and 380 mg/l for brines, with Li/Cl ratios of  $277 \times 10^{-5}$  and  $399 \times 10^{-5}$ , respectively.

This enrichment is attributed to leaching of nearby Tertiary and Quaternary volcanic materials. Average lithium content of river waters is 1.1-2.0  $\mu\text{g/l}$  (Hem, 1970), and Li/Cl ratios compare favorably with those of fresh waters, assuming an average chloride content of 8.3 mg/l for fresh water (Table 3).

Total concentrations of the minor constituents strontium, lithium, and iodide for all sampled waters are within the range anticipated for halite-solution waters. The formation waters of this study could not be distinguished from halite-solution brines by total concentration because of a wide range in values found in both types of waters. However, the weight ratios Br/Cl, I/Cl, and Li/Cl may have diagnostic value in characterizing brine source.

### Comparison of Saline-Water Sources

Several samples representative of the various saline water types are depicted by the Schoeller diagram in Figure 4, which compares the constituent distribution of the different sample groups. All oil-field brines appear as sodium-calcium-chloride waters with other constituents in smaller amounts, whereas halite-solution waters are of the sodium-chloride type. Oil-field brines examined were enriched in total concentrations of strontium, lithium, bromide, and iodide in comparison to non-oil-field waters. With exception of Salt Creek waters, the abundance order  $\text{Na} > \text{Ca} > \text{Mg} > \text{K}$  is followed.

Some characteristics of the waters sampled may be attributed to suspected intermixing of other waters or interaction with associated sediments and rocks. For example, the alluvial wells of Saline County, although deriving salinity from subsurface Permian halite, also experience effects such as bank storage from the Solomon and Smoky Hill rivers, occurring during heavy storm activity when streams become influent. Similarly, a lower Mg/Ca ratio for the Ness County oil-field brine in comparison to that of the Russell County oil-field brine (Fig. 4) indicates the Ness County sample may have been involved in dolomitization reactions with surrounding rock.

The waters of Salt Creek differ most significantly from other samples, primarily because of the large volume of fresh water present. The concentrations of calcium and strontium differ from the other brines, the low calcium indicating undersaturation with respect to gypsum and low strontium



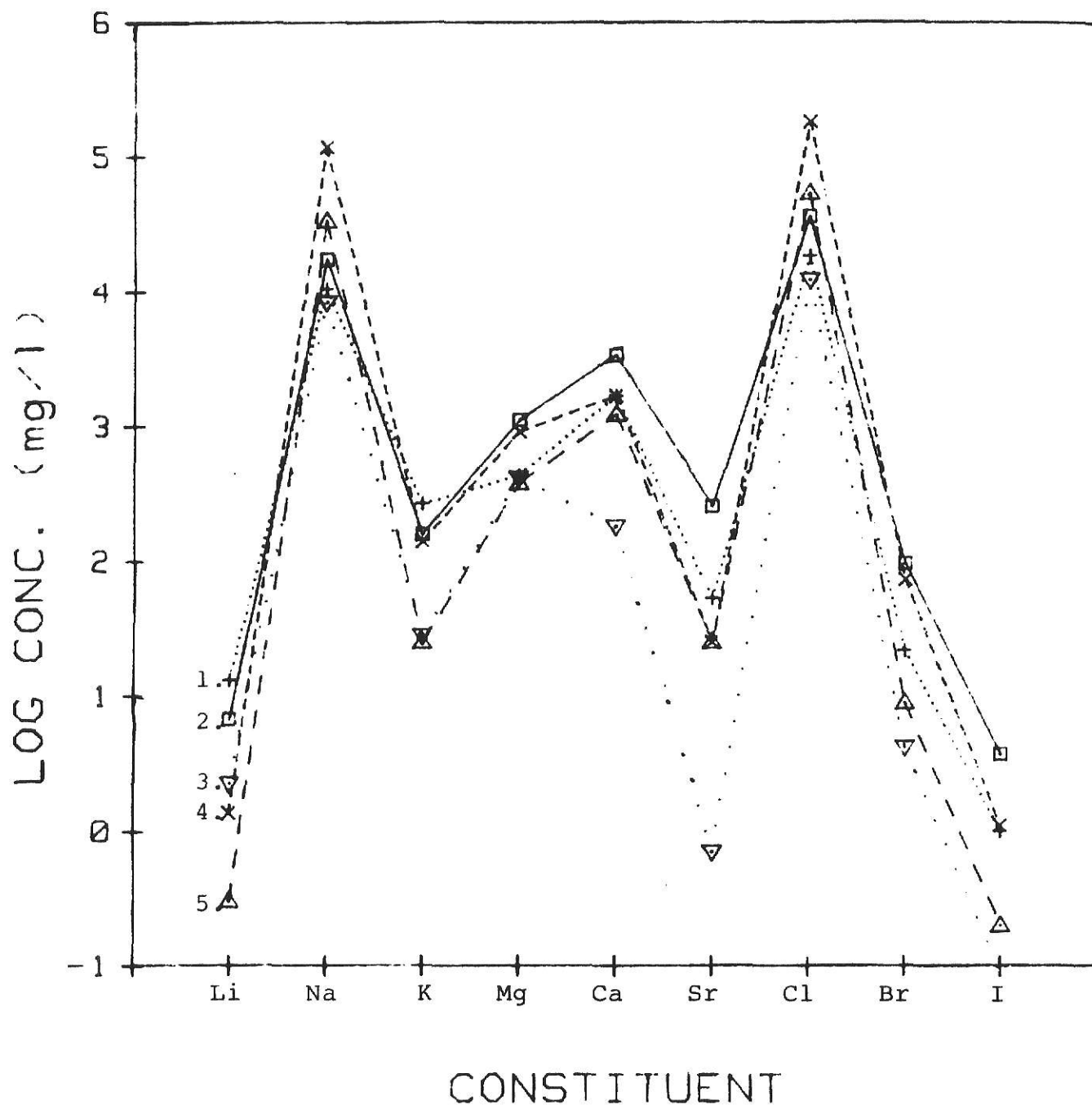


Figure 4. Schoeller diagram depicting constituent distributions for several brines of this study.

1. Oil-field brine, Ness Co.
2. Oil-field brine, Russell Co.
3. Salt Creek, Russell Co.
4. Halite mining solution, Hutchinson, Kansas.
5. Observation well, Saline Co.

typical of fresh waters, where concentration is limited by ion-exchange with calcium-bearing clays containing small amounts of strontium.

Generally, the weight ratios Br/Cl, I/Cl, Li/Cl, and Sr/Cl are significantly higher and the Na/Cl lower for oil-field waters than for halite solutions. Data in this study for formation and salt solution waters have a minimum Na/Cl ratio of 0.626, but Na/Cl ratios for oil-field brines range from 0.47 to 0.55. Values of Br/Cl ratios for oil-field brines ranged from  $5 \times 10^{-4}$  to  $33 \times 10^{-4}$ , whereas this value was generally less than  $5 \times 10^{-4}$  for non-oil-field samples. I/Cl ratios differ more appreciably, but indicate a preferred iodide enrichment for oil-field waters. For non-oil-field samples the I/Cl ratios were determined to be  $11 \times 10^{-6}$  or less; oil-field brines had values from  $50 \times 10^{-6}$  to  $150 \times 10^{-6}$ .

The ratio Li/Cl has great variability among particular types of waters, ranging from approximately  $7 \times 10^{-5}$  to  $84 \times 10^{-5}$  for oil-field waters, and  $0.50 \times 10^{-5}$  to  $18 \times 10^{-5}$  for other samples. Lithium distribution is suggested to be locally controlled by clay-mineral exchange reactions and by leaching or degradation of lithium-bearing minerals. The higher lithium of some oil-field waters may be attributed to contact with rock at one time enriched by lithium-bearing continental deposits.

As in the case of bromide and iodide the enrichment of strontium is indicated by high Sr/Cl values for oil-field waters. Strontium in brines may be controlled by dissolution

of carbonate rocks, gypsum, and other strontium-bearing minerals, by the formation of dolomite (strontium in the limestone will be expelled during conversion to dolomite), and by ion-exchange with clay minerals.

Because a direct comparison of weight ratios for minor constituents cannot differentiate brine sources, plots of these ratios versus chloride in mg/l were examined for separation of brine types. Plots of Li/Cl ratios versus Cl, Br/Cl ratios versus Cl, and I/Cl ratios versus Cl were anticipated to be most useful. In the case of I/Cl ratios versus Cl, the separation of oil-field brines from halite-solution brines was modified to I/Na ratios versus Cl because Na/Cl ratios were lower for oil-field brines than for non-oil-field waters.

Figure 5 depicts Li/Cl ratios versus Cl for saline waters of this study, selected oil-field brines from the Anadarko Basin in Oklahoma, and saline-formation waters from aquifer test wells in Stafford County, Kansas. The change in the Li/Cl ratio for seawater during evaporation to calcium sulphate and sodium chloride stages is indicated by a solid line in the lower right-hand portion of the graph (Collins, 1975). Generally, oil-field waters and non-oil-field waters fall into separate but adjoining zones, especially for waters containing 10,000 mg/l chloride or more. Halite-solution brines contain low lithium in relation to chloride, and plot in the field below or near the normal-evaporite curve. All oil-field brines plotted above this curve, indicating that diagenetic processes accompanying the formation of

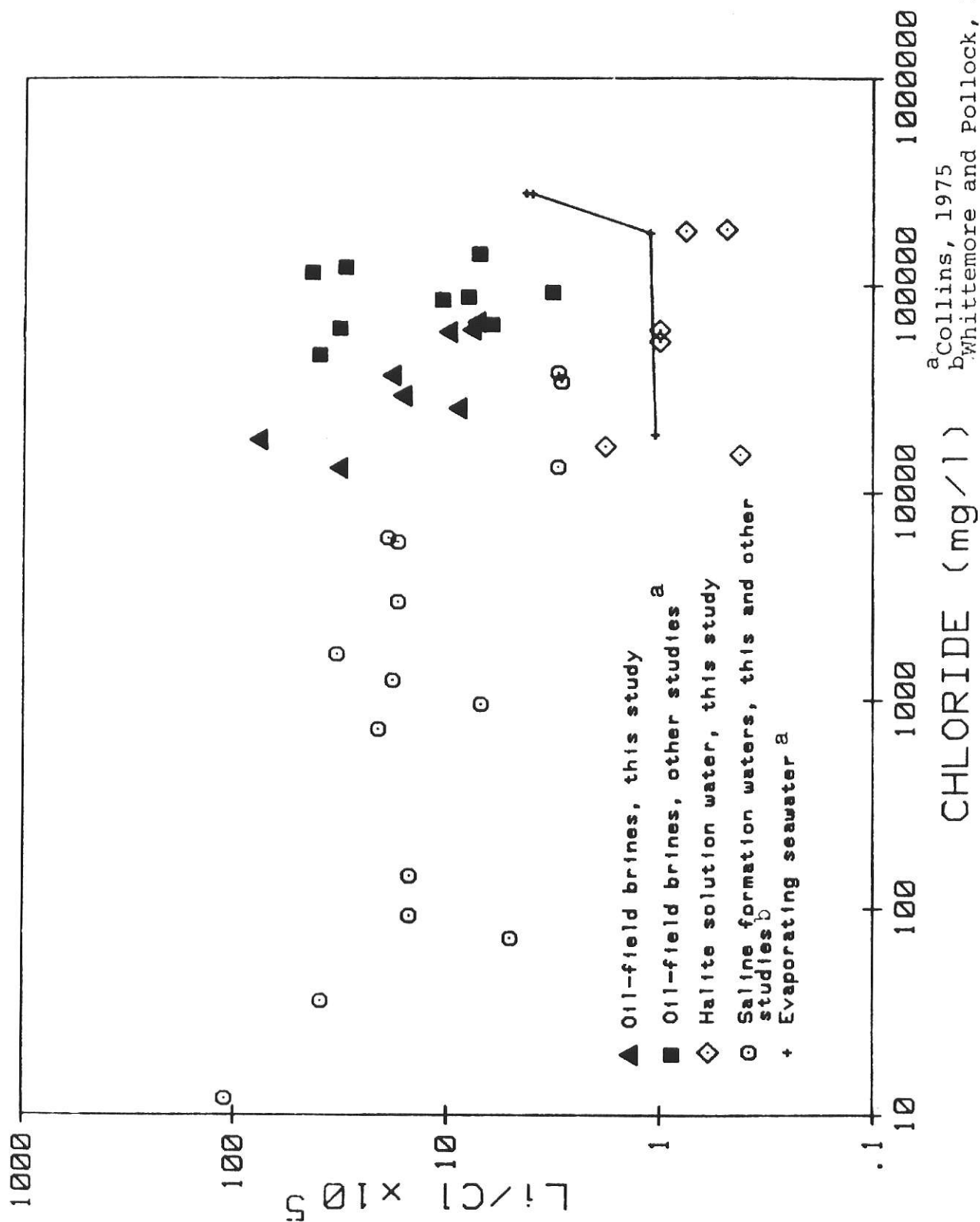


Figure 5. Li/Cl ratios versus chloride for salt waters of different sources.

petroleum deposits are conducive to lithium enrichment in surrounding brines. The scatter of points suggests varied factors such as solution of evaporites by oil-field brines, selective concentration by clay-membrane filtration, and exchange with clays during migration of the brines. Saline-formation waters are the most scattered throughout the field. In cases where there is fresh-water dilution, Li/Cl ratios will be higher, inasmuch as total chloride concentration decreases, and such waters would plot in the upper left-hand region of the graph.

The plots of Br/Cl ratios versus Cl and I/Na ratios versus Cl (Figs. 6 and 7) are more effective at depicting separation. The inert nature of bromide during brine evaporation has also allowed it to be used as a tool, coupled with divalent cation chlorides, in determining enrichment or loss of other constituents (Carpenter, 1978). Halite-solution waters and saline-formation waters follow a progression to regions below the seawater evaporation curve, suggesting in the case of halite-solution waters, that bromide is sometimes depleted in the parent evaporite itself, resulting in lower Br/Cl ratios. In the case of saline-formation waters, the geochemistry of bromide appears to be controlled by factors present during lithification of sediments.

The most effective separation of brine types is in the plot of I/Na versus Cl (Fig. 7). Oil-field waters lie in a zone appreciably distant from the seawater-evaporation curve and non-oil-field water zone. The non-oil-field data are

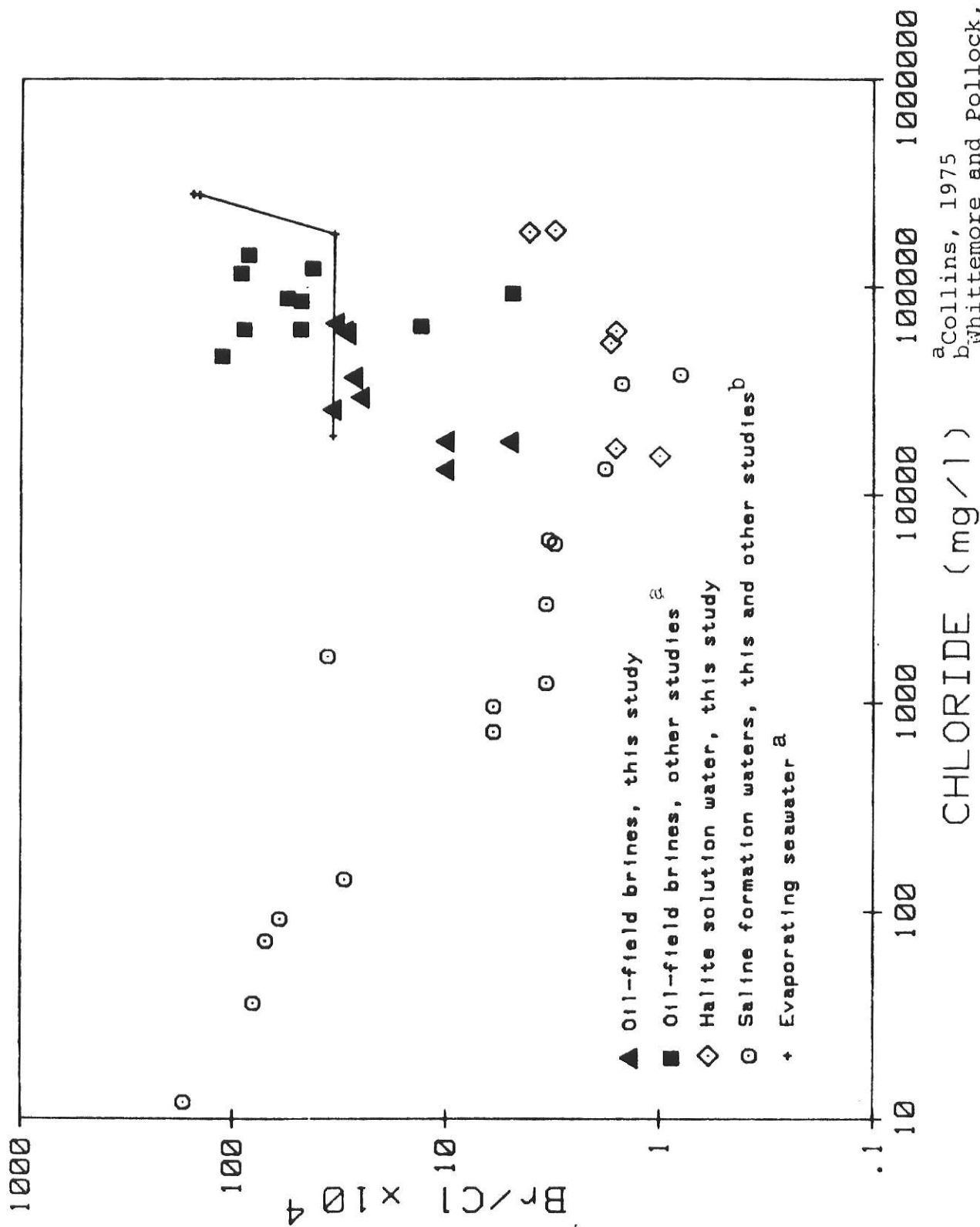


Figure 6. Br/Cl ratios versus chloride for salt waters of different sources.

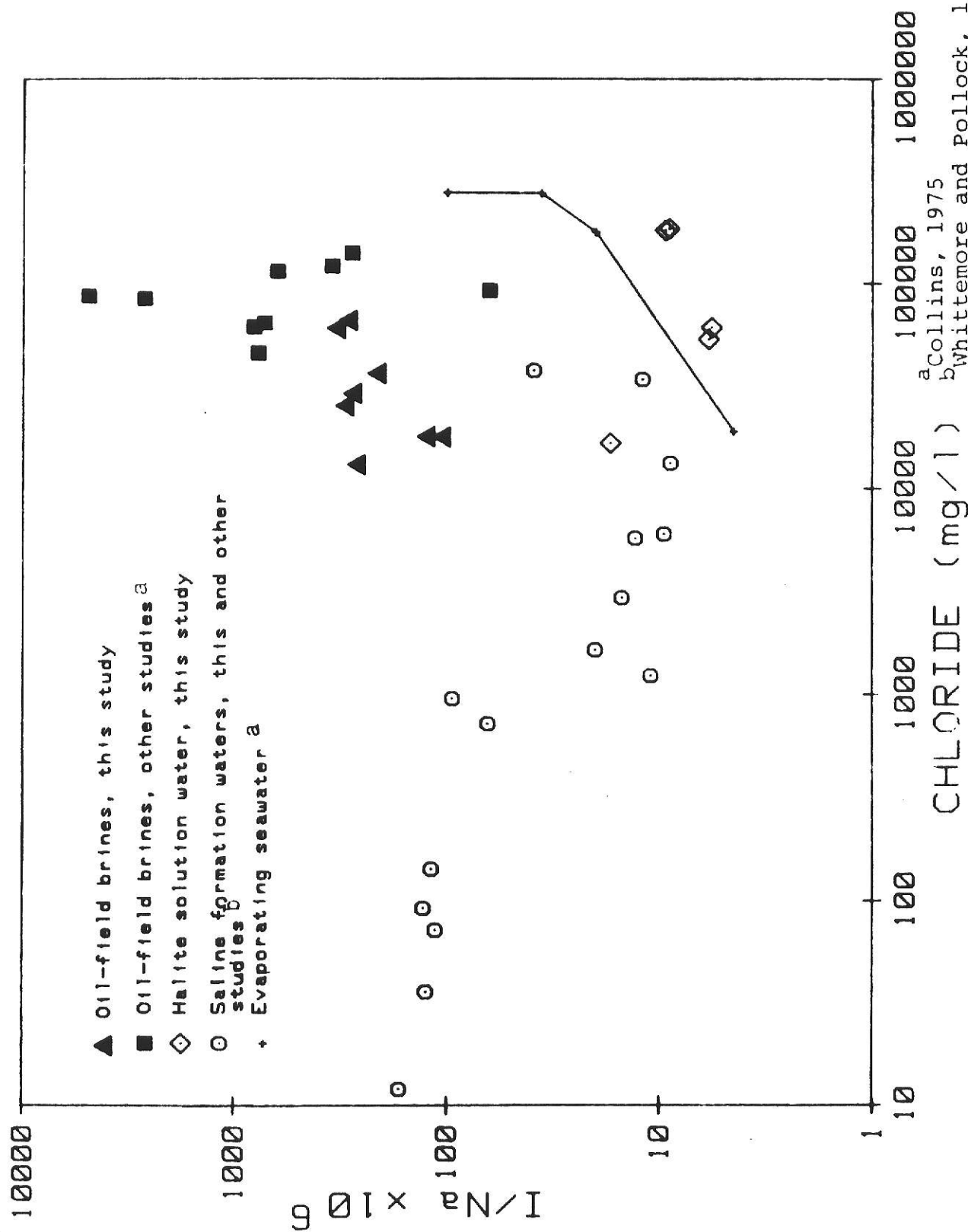


Figure 7. I/Na ratios versus chloride for salt waters of different sources.

more scattered and may be attributed to variations in I/Na ratios caused by mixing with fresh waters of varied sodium content and ion exchange of sodium on clays. Iodide solubility is also strongly controlled by the presence of organic material in sediment and water; increased adsorption of the iodide in the presence of organic material could also alter the I/Na ratio.



## SUMMARY AND CONCLUSIONS

Oil-field waters examined in this study are generally enriched in calcium and depleted in magnesium and potassium relative to brines produced by seawater evaporation. With exception of Ness County mid-Pennsylvanian-Mississippian waters, whose concentrations are similar to that of seawater, oil-field waters were enriched in chloride. All brines are strongly enriched in iodide, but bromide enrichment is more varied. Also, more varied is the enrichment of strontium and lithium.

Weight ratios of major constituents do not distinguish individual producing zones or different ages of zones. The same can be said in the case of ratios involving the minor constituents lithium, strontium, bromide and iodide, although such comparisons may be of use in a more detailed examination of a smaller region or of a more restricted stratigraphic sequence.

Halite-solution waters and saline-formation waters sampled are sodium-chloride brines containing minor amounts of accessory constituents. Total concentrations of bromide and iodide were much lower than for oil-field waters, and the ratios  $I/Cl$  and  $Br/Cl$  differed from oil-field waters in varied degrees. Ratios of  $Na/Cl$  for non-oil-field waters were higher, approaching and in some instances exceeding the 0.649 value for pure salt. Strontium and lithium, although

generally lower in salt-solution and formation waters, displayed strong variability within similar groups of samples. This is attributed to other parameters controlling solubility for these constituents.

A separation of oil-field from non-oil-field brine sources is best expressed by plots of I/Na ratios versus Cl and Br/Cl ratios versus Cl. Values for these plots indicate that the regions of oil-field and non-oil-field waters appear farther separated where chloride content is 10,000 mg/l or greater. This separation of zones may be of aid in suggesting salt sources for fresh water that is undergoing salinity increases. For example, a fresh-water source whose salinity is being contributed by oil-field brines would be expected to have higher I/Na, Br/Cl, and Li/Cl ratios at a given chloride concentration than ratios resulting from the mixing of fresh water with halite-solution brines.

Although processes controlling bromide and iodide enrichment in oil-producing reservoirs are complex and not fully determined, the original source of these constituents for Kansas oil-field waters is attributed to biogenic concentration by marine organisms. In many reservoirs, processes related to alteration of organic material to petroleum are conducive to bromide and iodide accumulation. Bromide and iodide for halite-solution waters and related formation waters is originally determined by equilibrium of precipitating salt with concentrated seawater. Variations in evaporites result from episodic variations in parent brine. Saline connate waters experience

alterations in bromide and iodide concentration by diagenetic processes (e.g. ion-filtration reactions with clay sediments) and by dilution. Carpenter (1978) suggested that most brines in sedimentary basins originated as interstitial fluid in evaporite deposits. These brines may then undergo a variety of chemical changes, related in many instances to the type of depositional environment and post-depositional history. The brines of different sources examined in this study indicate chemical alteration of both major constituents and minor elements.

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DETERMINATION OF SOURCES  
OF SALINE WATER IN KANSAS BY  
BROMIDE AND IODIDE GEOCHEMISTRY

by

Livia Juodisius Pollock

B.S., Cleveland State University, 1976

AN ABSTRACT OF A MASTER'S THESIS

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requirements for the degree

MASTER OF SCIENCE

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1982

## ABSTRACT

Saline waters from several sources in Kansas were analyzed to determine bromide, iodide, lithium, strontium, and chloride contents in order to characterize constituent variation among the different water types. Oil-field brine samples were collected from producing zones in Russell, Butler, and Ness counties; waters actively dissolving the Hutchinson Salt Member of the Wellington Formation (Permian) were taken from observation wells in Saline County, salt mining operations in Hutchinson, and a core sample from Lyons. The salinity of Salt Creek, Russell County, is attributed to salt seeps from the Dakota Formation, and creek waters were used to represent non-oil-field brine formation waters.

Oil-field waters generally showed higher bromide, iodide, lithium, and strontium than non-oil-field waters. Variation of weight ratios of these constituents to chloride concentration did not clearly distinguish the various sources of waters, although the ratio  $\text{Na/Cl}$  was consistently lower for oil-field waters. Plots of  $\text{I/Na}$  and  $\text{Br/Cl}$  ratios versus chloride concentration were found to be the most useful in differentiating petroleum-associated waters from halite-solution brines. Bromide and iodide distributions, although not diagnostic when used alone, are useful tools in distinguishing salinity source on a regional scale, in conjunction with other geochemical parameters.