

INFRARED SPECTROSCOPY OF PICLORAM INTERACTIONS WITH Al(III)-, Fe(III)-, AND Cu(II)-SATURATED AND HYDROUS OXIDE-COATED MONTMORILLONITE

Y. AOCHI AND W. J. FARMER

Department of Soil and Environmental Sciences, University of California, Riverside
Riverside, California 92521

Abstract—Thin clay films prepared from aqueous suspensions of the potassium or sodium salt of picloram (4-amino-3,5,6-trichloropicolinic acid) with Al-, Fe-, or Cu-saturated montmorillonite or with montmorillonite coated with hydrous oxides of Al, Fe, or Cu were examined in an air-dry condition by infrared (IR) techniques to elucidate possible modes of interaction between picloram and the mineral surfaces. Deuteration was used to confirm band assignments of picloram and its salts prior to interaction with montmorillonite. Picloram interactions with Al- and Fe-saturated montmorillonite and with montmorillonite coated with hydrous oxides of Al and Fe were concentration dependent. At high picloram concentrations similarities with the IR spectrum of potassium picloram indicated that much of the picloram was present in the salt form. As the concentration of picloram was reduced below that equivalent to 1 meq/g clay, the IR spectrum indicated the presence of the monomeric acid on the mineral surface. The spectrum of picloram on montmorillonite with a coating of copper hydrous oxide was similar to that of a Cu-picloram complex indicating coordination type bonding. The spectrum of picloram with Cu-saturated montmorillonite did not correspond to any of the other spectra of picloram examined. The interaction of picloram with montmorillonite coated with a hydrous oxide coating of Cu and with Cu-saturated montmorillonite were independent of picloram concentration in the range 2.20–0.44 meq/g clay.

Key Words—Adsorption, Hydrous oxides, Infrared spectroscopy, Montmorillonite, Picloram.

INTRODUCTION

In a previous paper, Farmer and Aochi (1974) concluded that the most important factor in the sorption of picloram (4-amino-3,5,6-trichloropicolinic acid) by several different soils was the organic matter content as it was the best indicator of the "effective pH" of a soil suspension. "Effective pH" was defined as the pH that results from summing the protons in solution and the protons available on the surface of the soil particles in the solution volume of the slurry. It was shown that increasing sorption upon increasing either the soil:solution ratio or the ionic strength was attributable to a higher effective acidity in the slurry and the corresponding increased formation of molecular picloram. Sorption was thus correlated with the amount of molecular picloram formed and subsequently bound by weakly acidic functional groups of organic matter.

This mechanism did not appear to be operative in the case of picloram sorption by clay minerals reported by Bailey *et al.* (1968). It seemed more likely that coordinate bonding between picloram and interlamellar cations of the clay was responsible. Arnold (1973) and Arnold and Farmer (1979) reported the pronounced effect of cation saturation on the sorption of picloram not only on clays but on different soils, exchange resins, and humic acids. Relative magnitudes of Freundlich k values of these materials were well correlated with coordinating ability of the cation involved. In all cases, saturation with Cu(II) resulted in a material of higher

affinity for picloram compared to materials saturated with other cations.

Arnold (1973) isolated a Cu(II)-picloram compound from an aqueous solution of CuCl_2 and the potassium salt of picloram. Based on elemental analysis and infrared spectroscopy (IR) of the resultant crystals, he proposed a bis-chelate structure involving coordination through both the annular nitrogen and the carboxylic acid group of picloram. Formation of such a chelate structure was expected to enhance the sorption of picloram on materials containing Cu(II). No evidence, however, was presented for the actual formation of this coordination compound on a soil material. This is obviously an area in need of further investigation.

In addition to the dependency of picloram sorption on soil pH, organic matter content, and the nature of the exchangeable cation, increased picloram sorption in soils has been correlated with the presence of hydrous iron and aluminum oxides (Hamaker *et al.*, 1966). In the present study, IR of thin clay films was used to observe the interaction of picloram with montmorillonite and with montmorillonite coated with hydrous oxides. IR has been used with great success to observe changes directly in functional group vibrations of organic compounds as they interact with thin clay films. Montmorillonite with its high surface area, high cation-exchange capacity (CEC), and ease of preparing self-supporting films has usually been the clay mineral of choice. Few studies, however, have utilized this

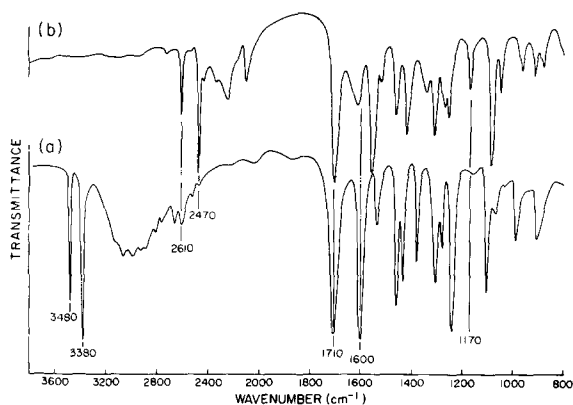


Figure 1. Infrared spectra of (a) picloram and (b) deuterated picloram.

technique for montmorillonite coated with hydrous oxides.

METHODS AND MATERIALS

Montmorillonite from Upton, Wyoming (API #25 obtained from Ward's Natural Scientific Establishment, Rochester, New York) was first saturated with Na using 1 N NaCl. The resulting monoionic clay was washed free of excess salts by repeated shaking and centrifugation with deionized water and the process completed with dialysis. The $<2\text{-}\mu\text{m}$ size fraction was used to obtain the Al(III)-, Fe(III)-, and Cu(II)-saturated clays by saturation with 1 N solutions of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, respectively. These were washed free of excess salt and stored as aqueous suspensions. The Al(III)-, Fe(III)-, and Cu(II)-saturated clays probably contained a portion of the metallic cations as the hydrous oxides due to hydrolysis of the cations.

Hydrous oxide coatings of from 0.5 to 8 meq/g were prepared using the method of Tullock and Roth (1975). An aliquot of the Na-saturated montmorillonite suspension was acidified to pH 2.5 with nitric acid. The weight of salt calculated for the desired coating of Al(III), Fe(III), or Cu(II) hydrous oxide was added while the suspension was rapidly stirred, and 0.2 N NaOH was added dropwise to adjust the pH of the suspension to 5.0–5.5. The salts of Al, Fe, or Cu used were the same as those used to prepare the monoionic clays of each cation. The resultant hydrous-oxide coated clay was washed repeatedly with deionized water until free of soluble salts and then diluted back to the original volume of the Na-montmorillonite. In this way, the amount of montmorillonite per unit volume was maintained fairly constant throughout the experiments. All concentrations were based on the weight of Na-montmorillonite rather than the hydrous-oxide coated material.

The reaction of picloram with monoionic clay or hydrous-oxide coated clay was carried out in aqueous suspension. Aliquots containing 25.2 to 28.2 mg of montmorillonite were equilibrated with solutions of the K or Na salt of picloram ranging in concentration from 2.07 to 10.4 meq/liter at ambient temperature. Picloram was added as a salt to allow a greater concentration range to be studied and is, in actual field situations, generally applied in formulations as a salt. Use of either the Na or K salt of picloram yielded the same results in this study. The total volume of the suspension was 6.0 ml, and the equilibration period was 24 hr with continuous shaking. After the equilibration period, 1.0-ml aliquots were removed and pipetted onto plastic film. When dry, the clay films were peeled off the plastic, and the IR spectrum was obtained for the air-dried, self-supporting clay films on a Perkin Elmer 621 Infrared Spectrometer. On the air-dry clay films, picloram concentrations ranged from 0.44 to 2.2 meq/g clay. Minimum concentrations of picloram observable by IR were strongly dependent on the particular clay material used.

Analytical standard picloram (Dow Chemical Corporation) was used throughout the experiment. Sodium and potassium picloram salts were obtained by titrating the acid with 0.2 N NaOH or KOH to pH 7.0. The solution was allowed to dry, and the salt was recovered. Deuteration of picloram and its salts was accomplished by recrystallization from a solution of deuterium oxide in a water-free nitrogen atmosphere. Examination of the spectra indicated complete deuteration of the amino and carboxylic acid groups of picloram. Spectra of the acid and the deuterated acid were obtained as Nujol, Fluorolube, or hexachlorobutadiene mulls so that monomer-dimer effects resulting from interactions with KBr discussed by Farmer (1957) could be avoided. The spectra are presented in this study as composites of these mull spectra to eliminate interference from mulling agent bands. Cu(II)-picloram was crystallized using the method described by Arnold (1973).

RESULTS AND DISCUSSION

Band assignments for picloram were made by comparing spectra of the acid, deuterated acid, and the potassium salt. Kuo (1973) presented extensive band assignments for picloram and its Na salt. Substantial differences exist between the interpretations of the IR spectra as presented by Kuo (1973) and the interpretations based on the evidence of the present study resulting in significantly different band assignments.

The spectra of picloram and its deuterated analog are presented in Figure 1. The general appearance of the spectra is much more in accord with those reported by Hadzi and Sheppard (1953) and Bratoz *et al.* (1956) for ordinary dimeric carboxylic acids than with those reported by Yoshida and Asai (1959) for pyridine carboxylic acids. The work of the former authors, therefore,

was used as the primary basis for the band assignments presented here.

Two sharp bands at 3380 and 3480 cm^{-1} are prominent in the high frequency area of the spectrum due to N–H-stretching vibrations. Adjacent to these bands are the broad νOH band centered around 3000 cm^{-1} and its main satellite bands at 2600 and 2660 cm^{-1} . Upon deuteration these bands shifted to 2470 cm^{-1} ($\nu\text{NH}/\nu\text{ND} = 1.37$) and 2610 cm^{-1} ($\nu\text{NH}/\nu\text{ND} = 1.33$) for νND , 2250 cm^{-1} ($\nu\text{OH}/\nu\text{OD} = 1.33$) for νOD , and 2105 cm^{-1} for the deuterated satellite band.

The carbonyl-stretching frequency of the carboxylic acid group of picloram in dimeric form was observed at 1710 cm^{-1} . Upon deuteration this band shifted only slightly to 1705 cm^{-1} . However, when picloram is dissolved in dioxane it should exist as a monomer rather than a dimer, and the $\nu\text{C}=\text{O}$ band is accordingly shifted to a higher frequency and appears as two bands at 1735 and 1760 cm^{-1} .

Neutralization of the acid with KOH resulted in the disappearance of the carbonyl band and the appearance of two carboxylate bands at 1600 and 1415 cm^{-1} . Both of these bands are coincident with or overlap at least one other band in the spectrum. This is a typical phenomenon observed in this "fingerprint" region, and only through comparison with spectra of the deuterated acid was it possible to clarify the band assignments.

As can be seen from Figure 1, deuteration of picloram resulted in the loss of the band at 1600 cm^{-1} , which was assigned to the N–H-bending mode (δNH), and the corresponding appearance of the δND band at 1170 cm^{-1} ($\delta\text{NH}/\delta\text{ND} = 1.37$). Because the appearance of the NH-stretching region indicated that deuteration was quite complete, the broad band remaining at 1615 cm^{-1} was assumed to be one not observable in the spectrum prior to deuteration. It was assigned to one of the five characteristic ring vibrations ($\nu\text{C}=\text{C}$) expected for a pyridine ring (Cross and Jones, 1969). The other four ring vibrations were assigned to the bands at 1550, 1465, 1425, and 965 cm^{-1} for deuterated picloram: analogous bands were observed at 1540, 1460, 1435, and 990 cm^{-1} for picloram itself. The variable intensities of these bands is well known. The radical change in the band intensities upon deuteration is apparent from Figure 1 and was observed also in the spectrum of the deuterated potassium salt of picloram. This phenomenon was noted previously by Hadzi and Pintar (1958) in their study of monomeric carboxylic acids.

The existence and expected position of the two coupled C–O-stretch/O–H-bending vibrations for dimeric carboxylic acids and their deuterated analogs was discussed at length by Hadzi and Sheppard (1953) and Hadzi and Pintar (1958). For picloram, these vibrations can be assigned by analogy to benzoic acid to the bands at 1378 and 1280 cm^{-1} which are replaced by two bands at 1050 and 1345 cm^{-1} upon deuteration. Because of the coupled nature of these vibrations, specific assignment

of corresponding bands in the deuterated and nondeuterated states is difficult and perhaps not meaningful (Hadzi and Pintar, 1958). The remaining two intense bands in the picloram spectrum at 1250 and 1308 cm^{-1} were assigned to $\nu\text{C}-\text{N}$. In the spectrum of the potassium salt, the latter band shifted to 1340 cm^{-1} and became very broad and intense.

The band assignments made for picloram and its salt were used to correlate the chemical structure of picloram with interactions on mineral surfaces. Montmorillonite was used to represent six different surface conditions. Three of these conditions were montmorillonite saturated with either Al(III), Fe(III), or Cu(II). The other three conditions were montmorillonite which had been treated with the hydrous oxide coatings of one of the same three cations. All reactions between montmorillonite and the mineral surfaces were carried out with the potassium salt of picloram in an aqueous suspension of the clays. After a 24-hr reaction period, the suspensions were allowed to air dry forming thin, self-supporting films for IR analysis.

The IR spectra of Al-saturated montmorillonite with four different concentrations of picloram are shown in Figure 2. The spectra cover the range from 1200–1800 cm^{-1} , the most informative part of the spectra. In other regions either the picloram spectrum was too weak to observe or was hidden by strong inorganic absorption bands. At the highest picloram concentration of 2.2 meq/g clay in Figure 2, the spectrum is essentially that of the salt of picloram as indicated by the presence of the two strong carboxylate bands near 1610 and 1420 cm^{-1} . As the level of picloram was reduced to 0.44 meq/g clay (Figure 2), several changes took place in the spectrum. There was a gradual reduction in the intensity of many of the peaks in the region between 1250 and 1650 cm^{-1} accompanied by a general shift to higher frequencies. At the lowest picloram concentration of 0.44 meq/g clay, the carboxylate peaks due to the salt of picloram were no longer present. The peak at 1420 cm^{-1} completely disappeared. The band at 1630 cm^{-1} is attributed to the N–H-bending vibration and to O–H-bending vibrations of any adsorbed water on the clay surface. At all picloram concentrations in Figure 2, IR absorption took place in the region between 1700 and 1780 cm^{-1} . As the concentration of picloram was reduced, this absorption became relatively more intense than other peaks at the lower concentrations and was resolved into three bands with the most intense band at 1720 cm^{-1} . These absorption maxima occur at a higher frequency than that of the carbonyl band for dimeric picloram and are evidence for the presence of the monomeric acid on the surface of the Al-saturated montmorillonite. Picloram dissolved in dioxane exhibited absorption maxima at both 1760 and 1735 cm^{-1} due to the carbonyl of the monomeric acid. The fact that three absorption maxima exist in the carbonyl region for picloram at low concentrations on Al-saturated

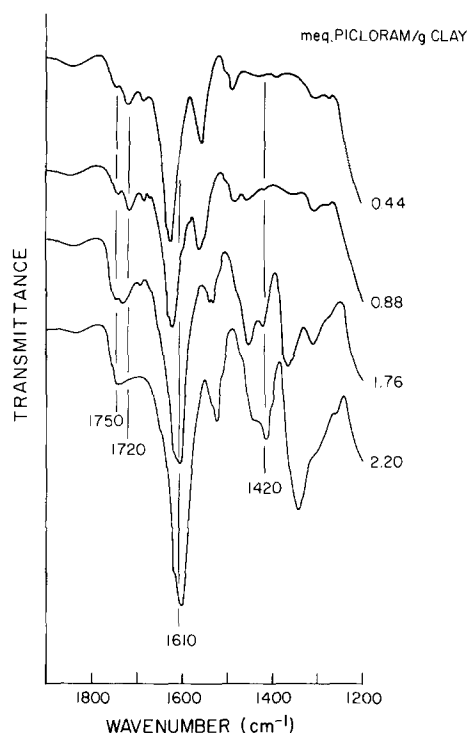


Figure 2. Infrared spectra, 1200–1800 cm^{-1} , of picloram on Al-montmorillonite. The picloram is present on the clay in increasing concentrations from 0.44 to 2.20 meq picloram/g clay.

montmorillonite suggests a more complex environment for the picloram than when it is dissolved in dioxane. Presumably, monomeric picloram was present on the clay surface even at the higher picloram concentrations with much of its spectrum masked by that of the salt form. The absorption in the range 1700–1780 cm^{-1} at the higher picloram concentrations in Figure 2 is attributed to monomeric picloram.

The same pattern of spectra was obtained for montmorillonite saturated with iron except that lower concentrations of K-picloram were necessary before shifts indicating interaction were obtained. Otherwise, the same bands at the same frequencies were observed. These results can be reasonably explained if picloram was attracted to the Al or Fe cation through a "water bridge" comprised of water molecules in the hydration sphere of the cation. The acidity of these water molecules, and therefore their ability to protonate the picloram anion to form the monomeric acid, is a function of the strength of their attraction to the cation. This mechanism was discussed at length by Mortland (1970). The interpretation of picloram sorption by Al- and Fe-saturated clay is complicated somewhat by the presence of hydrous oxides on the clays due to the hydrolysis of both Fe and Al during the preparation of the clays. The influence of hydrous oxides on picloram-clay interactions is considered later.

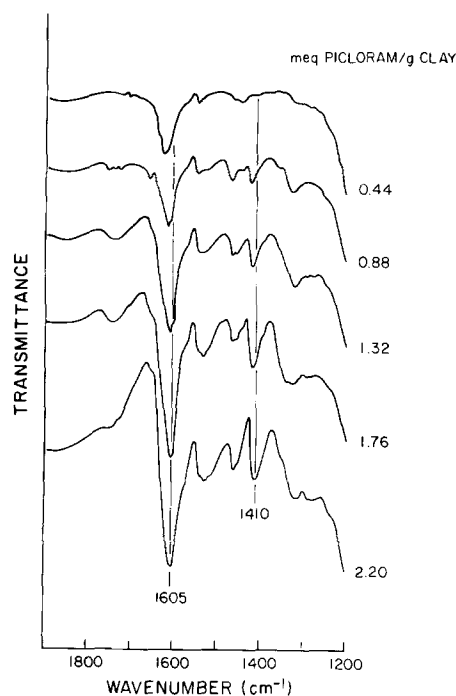


Figure 3. Infrared spectra, 1200–1800 cm^{-1} , of picloram on Cu(II)-montmorillonite. The picloram is present on the clay in increasing concentrations from 0.44 to 2.20 meq picloram/g clay.

The series for Cu-saturated montmorillonite (Figure 3) was not the same as for Al and Fe. The most striking aspects were the unchanging nature of the spectrum over a wide concentration range and the fact that band shifts indicative of interaction for Al- and Fe-saturated clays never appeared. This was rather puzzling in view of the reported reactivity of many Cu-saturated materials.

Hydrous oxides, both individually and in combination with other soil components, have received a great deal of attention in recent years. Excellent discussions of hydrous oxides—their formation, physical and chemical effects, structure, interactions with soil components, comparison of artificially created and naturally occurring materials—are contained in Dixon and Weed (1977). The many contradictory results reported in the literature concerning the effects and stability of synthetic hydrous-oxide coated clays were discussed at length by Keren *et al.* (1977) who attributed them primarily to differences in method of preparation.

Results using Na-saturated montmorillonite with coatings of 0.5, 2, 4, and 5 meq/g of either Al or Fe hydrous oxide and varying concentrations of K-picloram were similar to those with the respective Al- and Fe-saturated clays. The general effect of the hydrous oxide was to diminish the interaction of the clay with the picloram salt, i.e., lower concentrations were necessary to cause the same shifts in the IR adsorption bands. This effect could be caused by several factors. The su-

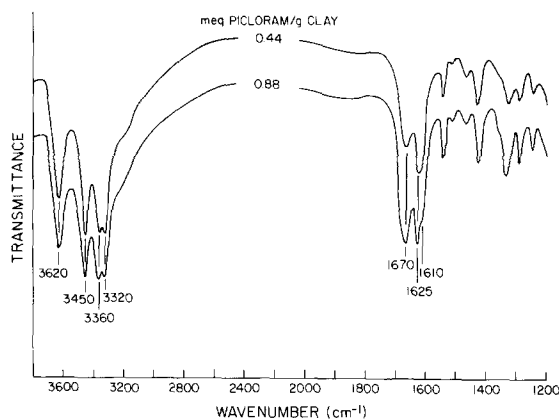


Figure 4. Infrared spectra of picloram on Cu hydrous-oxide coated montmorillonite.

pernatant pH of the clay suspension was in all cases considerably higher for the hydrous-oxide coated material than for the monoionic clays, thus, the acidity of the clay surface is less. If picloram-clay interaction occurs due to the formation and bonding of the molecular acid, reduction in this interaction would be expected to occur. Hydroxide ions would also be expected to compete for coordination sites around the cation. Another mechanism could be simply a reduction in surface area available for interaction. In any case, the general effect was to reduce the affinity of the clay surface for picloram rather than to increase it.

The excess retention of Cu on montmorillonite beyond the CEC of the clay was attributed to the precipitation of copper hydroxide on the surface of the clay (Bingham *et al.*, 1964). McBride and Mortland (1974) confirmed this conclusion and showed by electron spin resonance and magnetic susceptibility studies that Cu(II) is not specifically adsorbed by montmorillonite and does not bond with lattice OH. It exists rather as strongly hydrated $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ in suspension and as $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ within the air-dry clay lattice. Bingham *et al.* (1964) showed that precipitation of $\text{Cu}(\text{OH})_2$ occurs at pHs normally expected for soils.

When Na-saturated montmorillonite with a 5 meq/g coating of Cu hydrous oxide was reacted with varying concentrations of K-picloram, the results were distinctly different from any of the previous forms of picloram herein examined (Figure 4). The most striking features of the spectra in Figure 4 are: (1) the increased sharpness of all bands in the spectra, (2) the appearance of three sharp, intense bands at 3320, 3360, and 3450 cm^{-1} , and (3) the appearance of a band at 1670 cm^{-1} .

The increased sharpness of all bands in the spectrum compared to those observed for the other surface conditions studied seemed to indicate either the formation of a very ordered coating—perhaps almost crystalline in nature—on the surface of the clay or a more uniform layering of the clay platelets themselves. The three

sharp bands in the high frequency region of the spectrum are due to the presence of the hydrous oxide only. They were present in all spectra when coatings of 5 meq/g to 8 meq/g were used. It is also at these coating levels that an extra peak appeared at 5.47 Å in the X-ray diffraction pattern (XRD) of the clays. The same bands in the IR spectrum and the same peak in the XRD pattern were observed when the hydrous oxide was precipitated alone in the absence of clay.

The band at 1670 cm^{-1} in the spectrum of the Cu hydrous-oxide coated clay with picloram is assigned to a carbonyl group. With its appearance, the spectrum is almost identical to that of bis-Cu(II)-picloram (Arnold, 1973). Apparently, the coating of the hydrous oxide on the clay surface promoted the formation of the bis-chelate to rather high concentrations. The increasing prominence of the $\nu\text{C}=\text{O}$ band was accompanied by an increase in the suspension pH, in contrast to the Al- and Fe-hydrous oxide systems where the pH decreased as the concentration of K picloram increased. The formation of the coordination compound on the hydrous-oxide coated clay surface must occur with the displacement of hydroxide anions from the coordination sphere of copper. Elemental analysis of bis-Cu(II)-picloram reported by Arnold (1973) precludes the incorporation of hydroxyl in the isolated crystal itself. The role of the hydrous oxide surface seems to be one of shifting the picloram dissociation equilibrium away from the molecular acid, thus promoting the formation of the coordination compound. In the bis-Cu-picloram proposed by Arnold (1973), the Cu cation is coordinated through the annular nitrogen of the pyridine ring and one of the oxygens of the carboxyl group, leaving the carbonyl free to vibrate at 1670 cm^{-1} . The formation of such a chelate would be expected to enhance the sorption of picloram by materials containing Cu. Indeed, Arnold (1973) in separate sorption studies reported greatly enhanced sorption of picloram by soils, clays, and humic materials when Cu was present as compared to picloram sorption in the presence of a number of other cations.

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Резюме—Тонкие filmy глины, приготовленные из водных суспензий калиевой или натриевой соли пиклорама (4-амино-3,5,6-трихлоропиколиновой кислоты) с монтмориллонитами, насыщенными Al, Fe, или Cu либо монтмориллонитами, покрытыми гидроокисями Al, Fe, или Cu, были исследованы в условиях сухого воздуха при помощи инфракрасных техник (ИК), чтобы оценить возможные типы взаимодействия между пиклорамом и поверхностями минералов. Дейтеризация была использована, чтобы подтвердить принадлежность полос пиклорама и его солей перед взаимодействием с монтмориллонитом. Взаимодействия пиклорама с монтмориллонитами, насыщенными Al и Fe, и с монтмориллонитами, покрытыми гидроокисями Al и Fe, зависели от концентрации. При высоких концентрациях пиклорама подобия с ИК спектром калиевого пиклорама указывали на то, что большая часть пиклорама присутствовала в форме соли. Если концентрация пиклорама уменьшилась ниже 1 мэкв/г глины, ИК спектр указывал на присутствие мономерической кислоты на поверхности минерала. Спектр пиклорама на монтмориллоните, покрытом гидроокисью меди, был похожий на спектр комплекса Cu-пиклорам, указывая на координационный тип связи. Спектр пиклорама с монтмориллонитом, насыщенным Cu, не соответствовал какому-либо другому спектру исследованных пиклорамов. Взаимодействие пиклорама с монтмориллонитом, покрытым гидроокисью меди, и с монтмориллонитом, насыщенным Cu, не зависело от концентрации пиклорама в диапазоне 2,20–0,44 мэкв/г глины. [E.C.]

Resümee—Dünne Tonfilme, die aus wässrigen Suspensionen mit dem Kalium- bzw. Natriumsalz von Picloram (4-amino-3,5,6-trichloropicolinsäure) und Al-, Fe-, oder Cu-gesättigtem Montmorillonit bzw. mit Montmorillonit, der mit kristallwasserhaltigen Oxiden von Al, Fe, oder Cu umschlossen war, hergestellt wurden, wurden in lufttrockenem Zustand mit Hilfe von Infrarot (IR)-Spektren untersucht, um die möglichen Wechselwirkungsmoden zwischen Picloram und den Mineraloberflächen zu finden. Deuterisierung wurde verwendet, um die Bandenzuordnung des Picloram und seiner Salze vor der Wechselwirkung mit Montmorillonit zu bestätigen. Die Wechselwirkung von Picloram mit Al- und Fe-gesättigten montmorilloniten und mit Montmorilloniten, die mit kristallwasserhaltigen Oxiden von Al und Fe umgeben sind, waren von der Konzentration abhängig. Bei hohen Picloram-Konzentrationen zeigen Ähnlichkeiten mit den IR-Spektren von Kalium-Picloram, daß ein Großteil des Picloram in Salzform vorlag. Wenn die Picloram-Konzentration unter das Äquivalent zu 1 mÄqu/g Ton reduziert wurde, zeigte das IR-Spektrum, daß monomere Säure auf der Mineraloberfläche vorhanden ist. Das Spektrum von Picloram auf Montmorillonit, der mit kristallwasserhaltigem Kupferoxid überzogen war, war ähnlich dem eines Cu-Picloram-Komplexes, was auf eine koordinative Bindung schließen läßt. Das Spektrum von Picloram mit Cu-gesättigtem Montmorillonit entsprach keinen der anderen untersuchten Picloram-Spektren. Die Wechselwirkung von Picloram mit Montmorillonit, der mit einem kristallwasserhaltigen Cu-Oxid überzogen war, oder mit Cu-gesättigtem Montmorillonit waren im Bereich 2,20–0,44 mÄqu/g Ton unabhängig von der Picloram-Konzentration. [U.W.]

Résumé—De minces films d'argile préparés à partir de suspensions aqueuses du sel de potassium ou de sodium de picloram (acide 4-amino-3,5,6-trichloropicolinique) avec de la montmorillonite saturée de Cu, Al, ou Fe, ou avec de la montmorillonite recouverte d'oxydes hydratés d'Al, Fe, ou Cu, ont été examinés dans un état d'air-sec par des techniques d'infrarouge (IR) pour élucider des modes possibles d'interaction entre le picloram et les surfaces minérales. La deuteration a été utilisée pour confirmer les bandes assignées au picloram et avec ses sels avant l'interaction avec la montmorillonite. Les interactions du picloram avec la montmorillonite saturée d'Al ou de Fe et avec la montmorillonite recouverte d'oxydes hydratés d'Al et de Fe étaient dépendantes de la concentration. A de hautes concentrations de picloram, des similarités avec le spectre IR de picloram potassium ont indiqué qu'une grande partie du picloram était présent à l'état de sel. A mesure que la concentration du picloram était réduite sous celle équivalente à 1 meq/g d'argile, le spectre IR a indiqué la présence d'acide monomérique sur la surface minérale. Le spectre de picloram sur la montmorillonite recouverte d'oxyde de cuivre hydré était semblable à celui d'un complexe picloram-Cu, indiquant un lien de type coordonné. Le spectre de picloram avec la montmorillonite saturée de Cu ne correspondait à aucun autre spectre de picloram examiné. Les interactions du picloram avec la montmorillonite recouverte d'oxyde de cuivre hydré de Cu et avec la montmorillonite saturée de Cu étaient indépendantes de la concentration de picloram sur l'étendue 2,20–0,44 meq/g d'argile. [D.J.]