gray or brown, suggesting incomplete reduction of OsO$_4$. For example, reduction of 2-percent OsO$_4$ solution or OsO$_4$ vapor by thiourea gave a brown precipitate whereas thiosemicarbazide gave a black precipitate.

The properties of the reagents which are required for the various histochemical methods impose certain limitations on this new technique. If, for example, the products of the histochemical reaction before osmication have too great an affinity for lipid, the localization of the "osmium black" will reflect this shortcoming. In the continual redesign of reagents for perfecting histochemical methods for electron microscopy, it may become necessary to incorporate other groups for selective osmication in particular instances.

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Radium-226 and Polonium-210 in Leaf Tobacco and Tobacco Soil

Abstract. *Contents of radium-226 and polonium-210 in leaf tobacco and tobacco-growing soils vary with the source. The differences may result from production locality, culture, and curing. The polonium seems to be not entirely derived from the radium; plants probably take it up from the soil or air.*

Naturally occurring radioelements in manufactured tobacco and in smoke have been investigated many times. Earlier reports concern mostly beta activity of K^{40} (*1*), while recent studies mainly refer to alpha activity, especially of the radium and thorium series (*2*). The report on Po^{210} (*3*) is of special interest, for this element is volatile at the combustion temperature of manufactured tobacco.

Polonium-210 in tobacco plants is derived from either the soil or the air. It may be taken up directly from the soil or may result from radioactive decay of lead-210 or radium-226 taken up from the soil. It may also result from radioactive decay of the daughters of radon-222 deposited on the leaves. In re-examining the Po^{210} content of tobacco and in attempting to establish its origin, we studied the natural radioactivity in different types of leaf tobacco produced in various years in various localities. All samples had been stored in sealed glass containers or in hogsheads, without prolonged exposure to fresh air. Soils producing tobaccos in 1963 were sampled and tested for natural radioactivity in February 1964.

For determination of Po^{210}, 10-g samples of air-dried, finely cut tobacco were wet ashed in nitric acid with lead carrier. A sample was precipitated as the sulfate and chelated with ethylenediamine tetraacetic acid. The lead sulfide precipitated was dissolved in 3*N* HCl, and the Po^{210} was plated onto a nickel disc. The sample was mounted with ZnS phosphor, and the alpha particles, a measure of Po^{210} activity, were counted. With this technique the background is 0.01 count/min and the detection efficiency is 52 percent. The activity of the blank (0.04 count/min) has been subtracted from all Po^{210} data.

Quantitative measurements of Pb^{210} made by counting the beta activity of its Bi^{210} daughter failed because of the low activity, but beta activity data were qualitatively consistent with the Po^{210} analysis.

For Ra^{226} determination, 5 to 10 g of tobacco ash were fused with sodium carbonate along with barium carrier and Ba^{133} tracer. Barium and radium were separated from the calcium, and the barium was precipitated as the chromate and dissolved in perchloric acid. Recovery was determined by counting the gamma activity of Ba^{133} in the final solution, and radium was determined by counting the alpha activity of its gaseous daughter, Rn^{222}.

Natural activities found in the tobacco samples are shown in Table 1. Although lower than the others in Ra^{226} content, the 1938 tobacco samples also differ in type, growth locality, and culture and curing methods. There is a difference in Ra^{226} activity among flue-cured tobaccos from different areas. Tobacco from eastern North Carolina generally has lower Ra^{226} activity than that from Georgia. The same tendency is shown in Table 2 in the natural activity in tobacco-producing soils. The Ra^{226} content of soil samples from Tifton, Georgia, is higher than that of samples from Oxford, North Carolina. Fertilizer added to the soil may contribute in part to this difference. Sample No. 4, from a field continuously planted to burley tobacco, is high in available phosphorus and contains 2 to 3 times more Ra^{226} than the others. Similarly, sample No. 8, from a field continuously planted to tobacco and fertilized with 225 kg of P$_2$O$_5$ per hectare each year (200 pounds per acre), also has a higher Ra^{226} content.

Certain phosphate rocks contain

uranium; for example, the uranium content of clastic apatite from the land pebble phosphate field in Florida ranges between 0.011 and 0.032 percent in pebbles and between 0.0045 and 0.013 percent in pellets (*4*). In an early report by Moore (*5*), 3.3 pc of uranium (per gram) was found in igneous rock. One gram of uranium is in radioactive equilibrium with 3.3 $\times$ 10^{-7} g of Ra. Fertilizers containing uranium and its daughters would contribute to the higher level of Ra^{226} in soil.

Table 1. Natural radioactivity in tobaccos.

Tobacco type	Year produced	Activity (pc/g) (A) Measured Ra^{226} (May 1964)	(B) Calc. Pb^{210} from Ra^{226} (May 1964)	(C) Calc. Pb^{210} from Po^{210} (At harvest)	(C/A) Pb/Ra	(D) Measured Po^{210} (May 1964)
			Air-cured			
Maryland	1938	0.059±0.038*	0.03	0.27	4.6	0.15±0.01*
Pennsylvania cigar	1938	0.059±0.006	0.03	0.32	5.4	0.17±0.01
			Flue-cured			
Georgia (Tifton only)	1950	0.31±0.002	0.11	0.46	1.5	0.41±0.01
	1950	0.37±0.26	0.13	0.54	1.5	0.48±0.01
	1963	0.15±0.011	0.004	0.41	2.7	0.40±0.02
Georgia (mixed)	1959	0.39±0.002	0.06	0.27	0.7	0.30±0.01
	1960	0.30±0.016	0.03	0.25	0.8	0.25±0.01
	1961	0.30±0.008	0.02	0.42	1.4	0.40±0.01
	1962	0.21±0.018	0.01	0.36	1.7	0.35±0.03
	1963	0.30±0.018	0.008	0.42	1.4	0.42±0.06
East North Carolina	1955	0.15±0.002	0.04	0.28	1.9	0.25±0.03
	1956	0.14±0.000	0.03	0.38	2.7	0.33±0.02
	1959	0.19±0.001	0.03	0.37	1.9	0.35±0.14
	1960	0.25±0.007	0.03	0.41	1.6	0.39±0.03
	1961	0.16±0.007	0.01	0.51	3.2	0.48±0.01
	1962	0.14±0.013	0.008	0.45	3.2	0.43±0.03
	1963	0.16±0.011	0.004	0.31	1.9	0.30±0.01

* Error terms are one standard deviation calculated from two measurements of each radium sample and at least three measurements of each Po^{210} sample.

Table 2. Natural radioactivity in tobacco soils.

Soil sample	Description	Sample No.	Activity in May 1964 (pc/g) Ra^{226}	Po^{210}
	Air-cured area			
Quincy, Florida	Wrapper cigar field	1	0.60±0.10*	0.54±0.06
		2	0.67±0.04	0.39±0.02
		3	0.61±0.07	0.46±0.04
Greeneville, Tennessee	Waynesboro silt loam, continuing Burley tobacco, high available phosphorus	4	1.53±0.25	1.01±0.11
	Flue-cured area			
Tifton, Georgia	Tifton sandy loam, 3-year rotation experimental field, 225 kg P_2O_5 per hectare per year for tobacco only	5	0.79±0.06	0.30±0.01
	Tifton sandy loam, 2-year rotation, 180 kg P_2O_5 for tobacco only	6	0.76±0.02	0.37±0.003
	Klej loamy sand, 3-year rotation experimental field, 205 kg P_2O_5 for tobacco only	7	0.64±0.00	0.33±0.005
	Norfolk sandy loam, continuing tobacco, 225 kg P_2O_5 yearly	8	1.32±0.12	0.40±0.01
Oxford, North Carolina	10 years continuing tobacco experimental field, 100 kg P_2O_5 yearly	9	0.52±0.07	0.26±0.005
Florence, South Carolina	2-year rotation experimental field, 270 kg P_2O_5 per year for tobacco only	10	0.91±0.30	0.55±0.02

* Error terms are one standard deviation calculated from two measurements of each radium sample and at least three measurements of each Po^{210} sample.

The natural abundance of Ra^{226} in soil is about 1 pc/g (*6*). In soils from North Carolina, Moore (*5*) reported Ra activities of 0.54 and 0.45 pc/g in Cecil clay and in Durham sandy loam, respectively. These were top soil samples and were treated with hydrofluoric and sulfuric acids before fusion. These data agree well with the results in Table 2. Variations in the Ra content in soil could result from origin of the soil, sampling depth, and method of analysis.

The equilibrium activity of Pb^{210}, which is a daughter of Ra^{226} and a precursor of Po^{210}, may be calculated from either radionuclide. If the Pb^{210} at harvest calculated from Po^{210} is compared with that calculated from Ra^{226}, one finds that Ra^{226} is not the only source of Pb^{210} in tobacco.

The natural abundance of Rn^{222} is 50 to 200 pc/m^3 (*7*). Caldecott and Snyder (*8*) found that every one of hundreds of soils they tested generated radon, regardless of origin, depth, or intensity of weathering. The radon-generating power of clay mineral increased with increased moisture content up to 19.6 percent. Very little radon was released at moisture contents greater than 30 percent. Radium associated with clay fractions of soil was completely mobile. Even after the exchangeable radium had been removed, soils still retained a power to generate radon. As shown in Table 2, Po^{210} in the soil is not in equilibrium with Ra^{226}, indicating the escape of Rn^{222} into the atmosphere.

Radioelements were claimed to be necessary nutrients for plants (*9*). Photosynthesis in chlorophyll-containing cells was reported to be greatly stimulated by exposure to beta and gamma rays (*10*), and tobacco plants so treated weighed 684 g as opposed to 316 g, the weight of control plants.

A seasonal variation in the Ra content of the reservoir water and of plants was noticed (*11*). Very widely ranging values of radium were found in various plant tissues (*12*). Brazil nuts, known to be able to concentrate radium in the seed, contained more than 30,000 pc/kg, although the soil had an alpha activity of only 22,000 to 24,000 pc/kg (*13*). The amount of radioactivity found in the nut endosperm indicated a preferential retention of radium in some stem tissues during the process of upward transfer to leaves and to its subsequent release at the time of fruit formation. Drobkov (*14*) reported an increase in the intake of uranium by plants during blooming and maturation; he further stated that, while radioelements are distributed throughout the whole plant, they concentrate at the growing points, leaves, and fruit-bearing organs.

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Vibrational Excitation in Some Four-Center Transition States

Abstract. *The rates of substitution of deuterium for hydrogen in homogeneous gas phase reactions between* D_2 *and* HX (X = H, Cl, NH_2, *or* HS) *were measured at high temperatures by single-pulse shock tube techniques. The magnitudes observed and their dependency on concentration indicate that the rates of exchange are much faster than would be attainable were the deuterium to dissociate and the D atoms to react with HX by atomic displacement to produce H + DX. Also, these rates were not limited by methathesis through four-center transition states generated by sufficiently energetic collisions between the principal reactants. The results are compatible with the assumption that the rates are controlled by the populations of* D_2 *in about its 6th vibrational energy level.*

The model system for a methathesis reaction in the gas phase is:

$$H_2 + D_2 \rightarrow 2\,HD$$

Soon after the discovery of deuterium this reaction was studied both in a fixed volume and in hot tube flow reactors (*1*).

Under these conditions it was demonstrated that the reaction involves a dissociation

$$H_2 \leftrightarrows 2\,H$$

which is relatively slow in the gas phase but is assumed to be effectively catalyzed by the walls of the reaction vessel and to reach equilibrium rapidly, and an atomic displacement

$$H + D_2 \rightarrow H \cdots D \cdots D \rightarrow HD + D;$$

$$D + H_2 \rightarrow D \cdots H \cdots H \rightarrow HD + H.$$

This step, which designates a chain process, determines the rate of exchange. The second step is the classic prototype for the linear three-center transition state (H··H··H), the one for which theorists concerned with absolute reaction rates computed their first potential energy surfaces and estimated on an absolute basis the rate of the overall reaction (*2*). It appears that the four-center exchange mechanism was shunted by the three-center mechanism because of the rapid attainment of the dissociation equilibrium on the walls of the containing vessels. Under those conditions the overall activation energy is about 59 kcal/mole, of which 52 kcal comprises half of the dissociation energy of the hydrogen (required for the first step), and the remaining 7 kcal is the required activation energy for the atomic displacement (second step).

During the past 2 years the single-pulse shock tube (SPST) has been developed into an effective tool for studies of homogeneous gas phase kinetics (*3*). One may thus expose a sample of gas (the species of interest highly diluted with argon, 90 to 99 percent) to a temperature pulse of known intensity and duration (dwell time), under completely homogeneous conditions, such that wall effects are negligible. Indeed, the shock tube walls are at room temperature and therefore cannot be a source of atoms, as is unavoidably the case when the necessary heat influx comes through the walls of the vessel. Several H-D exchange reactions have been studied in this manner (*4*).

However, when we first attempted to analyze the results from the pairs of reactants, (H_2 + D_2) and (HCl + D_2), we encountered perplexing inconsistencies. The rate constants calculated on the basis of a bimolecular process involving a four-center transition state were scattered to a greater extent than is generally observed for experiments with single-pulse shock tubes (see *5*); the magnitudes for these rate constants were 10 to 100 times larger than the maximum computed from bimolecular collision theory. Finally, the data obtained at high temperatures were not compatible with results obtained by conventional techniques, in view of the lower apparent activation energies deduced from our shock tube runs.

The key to the puzzle was provided by the study of H-D exchange between (D_2 + NH_3) and (D_2 + H_2S) (*6*). In both cases the rate of production of HD followed the relation:

$$d(HD)/dt = k(Ar)(D_2), \qquad (1)$$

being *zero order* in NH_3 or H_2S. Hence, the step controlling the rate cannot be the bimolecular encounter between the principal reactants. In both cases it